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Volume 9—Adsorption

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KARLSRUHE, FEDERAL REPUBLIC OF GERMANY
1975

MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH & DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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16. ABSTRACT

In the summer of 1975 a Conference was held at the Engler-Bunte-Institute in Karlsruhe, Federal Republic of Germany on the subject of adsorption and reactivation as a water treatment unit process. Twenty-four papers were presented by the leading scientists and engineers in Western Europe. The Proceedings of this Conference have been translated and are presented herein. The information on the adsorption process formerly available only in German is now available in English. Copies of the previous 8 volumes are available in German from the Engler-Bunte-Institute.

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Volume 9 - Adsorption

Edited by

H. Sontheimer
University of Karlsruhe

Conference Held in
Karlsruhe, Federal Republic of Germany
1975

WATER SUPPLY RESEARCH DIVISION
MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Resarch Laboratory develops new and improved technology and systems for the prevention, treatment and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

In the summer of 1975 a Conference was held at the Engler-Bunte-Institute in Karlsruhe, Federal Republic of Germany on the subject of adsorption and reactivation as a water treatment unit process. Twenty-four papers were presented by the leading scientists and engineers in Western Europe. The Proceedings of this Conference have been translated and are presented herein. The information of the adsorption process formerly available only in German is now available in English and this should help those in the United States attempting to provide safe drinking water. Copies of the previous 8 volumes are available in German from the Engler-Bunte-Institute.

Francis T. Mayo
Director
Municipal Environmental Research
Laboratory

PREFACE

When I visited the Engler-Bunte-Institute in Karlsruhe, Federal Republic of Germany in the fall of 1975 Professor Sontheimer showed me the program of a recent conference on the treatment of drinking water for the removal of organic matter. As we discussed the various papers I realized that most of the European technology we had been seeking over the past few years was summarized at this Conference. We then dicussed how best to share this information with our United States colleagues. Translation of the Proceedings of the Conference seemed the best method.

After many hours of effort by Professor Sontheimer and his colleagues Dr. C.N.S. McLachlan, Dr. W. Kühn and Mrs. I. Hein, as well as by Dr. James M. Symons of my staff, the translation was completed and I am pleased to make it available. I am sure that all will agree that it represents a significant contribution to our literature.

Gordon G. Robeck
Coordinator, Water Supply Research
U.S. Environmental Protection Agency
Cincinnati, Ohio
November 1976

This publication was compiled in cooperation with many scientists. To all of them who have helped towards its completion I express my cordial thanks. I hope that this publication will contribute to the further development of adsorption processes and their optimum application. This, in turn, would be an important contribution towards ensuring the supply of drinking water of high quality at any time.

Thanks are due to all authors for agreeing to the translation of their papers and for their support to Mrs. I. Hein, Dr. C.N.S. McLachlan and Dr. W. Kühn for their valuable help in translating.

Prof. Dr. H. Sontheimer
Engler-Bunte-Institute
Karlsruhe, Federal Republic of Germany
August 1976

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CONVERSIONS FACTORS

1) AE (Angstrom) x 0.0001 = μmeter

2) Bar x 33.3 = feet of water
x 14.5 = pounds per square inch

3) cm x 0.39 = inches

4) Dates are Day/Month/Year

5) DMarks x 0.39 = Dollars

6) DMarks/kg x 0.18 = Dollars/pound

7) DMarks/m^3 x 1.1 = cents/cubic foot
x 147.7 = cents/1000 gallons

8) DMarks/t (metric) x 0.022 Cents/pound

9) Dollars/m^3 x 379 = cents/1000 gallons

10) Dollars/m^3/day x 3800 = Dollars/mgd

11) Dutch ¢/m^3 x 1.42 = cents/1000 gallons

12) g/cm^3 x 62.3 = pounds/cubic foot

13) g/m^3 x 1 = milligrams/liter (ppm)

14) Kcal/kg x 1.80 = BTU/pound

15) kg x 2.2 = pounds

16) kg/m^3 x 0.063 = pounds/cubic foot

17) kg/sec x 190,480 = pounds/day

18) km x 0.62 = miles

19) m x 3.28 = feet

20) m^2 x 10.79 = square feet

21) m^3 x 264 = gallons
x 35.3 = cubic feet

22) mbar x 0.0333 = feet of water
x 0.0145 = pounds per square inch

23) m^3/d x 0.000264 = million gallons/day

24) mg/m^3 x 0.000063 = pounds/cubic foot

25) m/hr x 0.4 = gpm/sq ft
x 0.055 = feet/second

26) m^3/hr x 4.4 = gallons per minute
x 0.0063 = million gallons/day

27) $m^3 H_2O$/kgGAC x 120 = gallons/pound GAC

28) mm x 0.039 = inches

29) mmole/m^3 x 0.001 = mmole/liter

30) mole/kg x 0.454 = mole/pound

31) m/sec x 3.28 = feet/second

32) m^3/sec x 22.8 = million gallons/day
x 35.3 = cubic feet/second

33) t(metric) x 0.91 = U.S. Ton

1

THE IMPORTANCE OF ADSORPTION PROCESSES IN DRINKING WATER TREATMENT

by H. Sontheimer

The use of adsorption as a purification process has become increasingly important for drinking water treatment in recent years. However, it is by no means a new technique, as may be seen in the following recommendation in a Sanskrit text from about 200 B.C.: "It is good to keep water in copper vessels, to expose it to sunlight, and filter it through charcoal" (MANTELL 1951).

Many centuries later NICHOLSON (1806) gave an exact description for using powdered charcoal and barrels with a charred inner surface for keeping water fresh on ships. At the same time the first carbon filters in waterworks were installed, using wood charcoal and bone charcoal. This kind of treatment was discontinued later because of the poor effectiveness of the filters (KIRK 1964).

With the development of processes for manufacturing suitable activated carbons, the importance of adsorption techniques for water treatment increased again. The removal of taste and odour and dechlorination were the most important aims during this period (HOLLUTA 1954, BAUER and SNOEINK 1973, SONTHEIMER 1975). In recent years, there has been an increased use of adsorption processes, mainly due to the rise in chemical water pollution (SONTHEIMER 1975). Adsorption plants such as activated carbon filters are no longer used for the removal of taste and odour but also for the reduction of the total load of organic substances, and especially of organic contaminants which are hazardous to health.

However, adsorption is only one possibility for the removal of dissolved organics in water treatment. It must compete with other treatment techniques which have the same objectives. These techniques are the following:

biological oxidation

chemical oxidation

precipitation and flocculation

ion exchange

membrane processes

One can distinguish between treatment methods based on chemical reactions, like oxidation processes and ion exchange, and those where accummulation of material on a solid surface takes place, like adsorption and flocculation. The latter two processes are the subject of this book.

All these processes have one thing in common: they are of limited effectiveness. Of the great variety of organic substances present in the water to be treated, only a certain fraction can be removed by such processes. Thus biological treatment in general removes only biodegradable material and, similarly, chemical oxidation cannot completely remove all organics. This is also the case in all the other treatment processes, including adsorption.

Therefore it is necessary to check for each water which treatment process is most essential,and the advantages and disadvantages of each process must be considered. Adsorption processes have the following advantages:

1. Specific removal of the least desirable organics, because they are usually strongly adsorbed.

2. Highly effective purification, especially while using activated carbon filters.
3. Favourable economics and simple application.

Of the points mentioned above, the specific adsorption characteristics of the undesirable organics are of special importance, since they are the main reason for the high treatment results and the reasonable economics. The question then arises which contaminants need to be removed in drinking water treatment and what specific characteristics the adsorbants need to have. Some papers in this book will deal with this problem because it is evident and of increasing importance for all waterworks. However, first of all a general view is given of the problems facing waterworks, starting with the discussion of analytical results obtained by the Engler-Bunte-Institut for the waterworks along the Rhine.

The most simple parameter to determine is the overall concentration of dissolved organics. Such measurements have been made along the Rhine at many sampling stations for some years. The values obtained are reported in the papers of the Association of the River Rhine Waterworks (ARW 1970-1971) and the Association of Waterworks at the Lake of Constance and the Rhine (AWBR 1970-1974). Fig. 1 shows the geometric mean data for three typical points along the Rhine.

Fig. 1: Organics in Rhine water.
Comparison of the geometric mean data for 1970-1974

The following sum parameters are shown: DOC (Dissolved Organic Carbon), COD (Chemical Oxygen Demand) and UV extinction. The total load of organic carbon may be obtained by measuring the DOC, COD or the UV extinction. The level of these values and thus the concentration of dissolved organic material in the

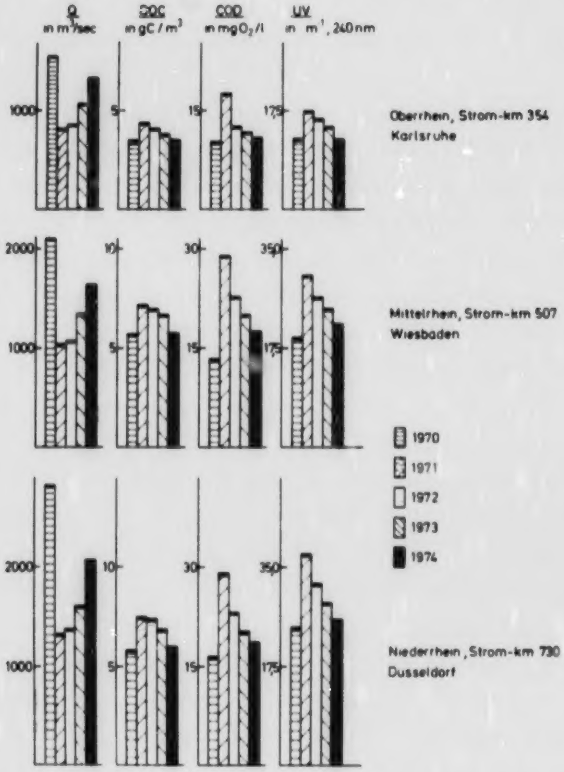

Fig. 1:

Oberrhein, Strom km 354: Upper Rhine at km 354 of the river
Mittelrhein : Middle Rhine
Niederrhein : Lower Rhine

river Rhine changes, as these data show, with flow rate and flow distance. However, it may be seen that the changes in the three parameters are not parallel.

Fig. 2: Comparison between DOC discharge and flow rate for some places along the Rhine (averaged curves 1970-1974)

Figure 2 shows particularly clearly how strongly the change in organic loading depends on the two parameters flow rate and flow distance. It may be seen that the DOC load increases both with increasing flow rate and with increasing flow distance. Conversely, the concentration shows the reverse tendency, that is to say, the highest concentrations are found at low flow rates.

Relationships such as shown in Figure 2 can be taken in conjunction with suitable theoretical models to give some information on the fraction of bioresistant compounds in the Rhine river water. These compounds are of special interest because they are not retained by the river bank filtration. Since most German waterworks at the Rhine do not take their raw water directly out of the river, these compounds have to be removed on the activated carbon filters.

Fig. 3: Change of load with bioresistant compounds with the flow distance

The increase in the load of bioresistant compounds with the flow distance is much higher than the increase of the water flow. Therefore, at the middle and lower Rhine river a high concentration of organic material has to be removed by adsorption. The chemical composition of these organics and the change in their relative fractions with flow rate is shown in Figure 4, using different group parameters and the data of 1974 (SONTHEIMER 1974).

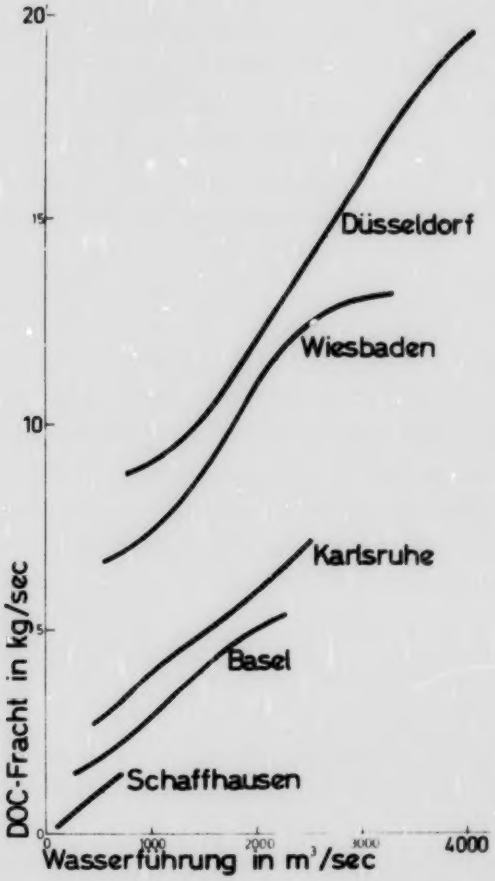

Fig. 2:

DOC-Fracht in kg/sec: DOC loading in kg/sec

Wasserführung in m^3/sec: flow rate in m^3/sec

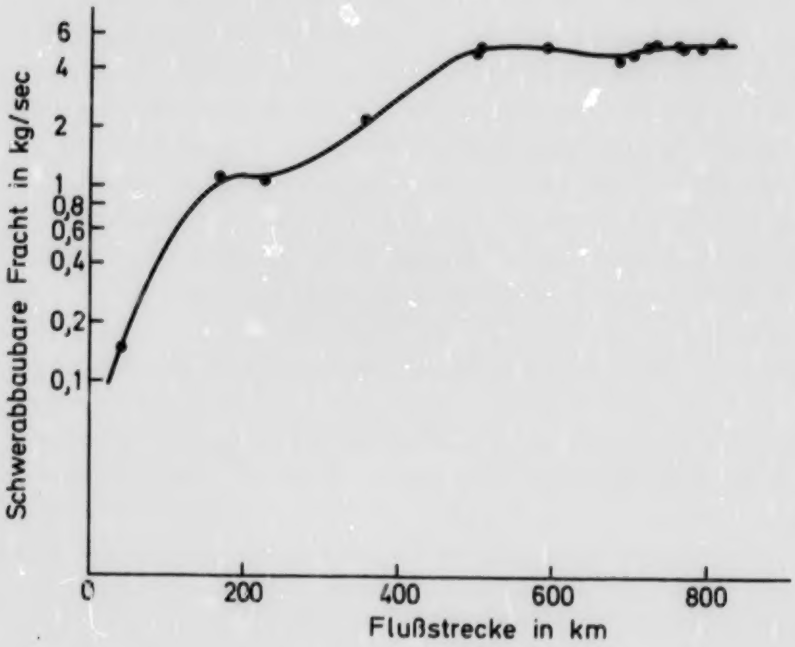

Fig. 3:

Schwerabbaubare Fracht in kg/sec: bioresistant load in kg/sec
Flußstrecke in km: flow distance in km

Fig. 4: Variation of the main components of the dissolved organic material with river flow rate in the lower Rhine

During ground passage, i.e. sand bank filtration, the biodegradable compounds and also part of the humic acids are removed. The substances remaining for the adsorption treatment belong mostly to the group of sulphonic and lignin sulphonic acids, which are only partly removed in sand bank filtration, and the organo-chloro compounds. These amount from 5 to 12 per cent of the total load and many of them are health hazards. That they can be adsorbed by activated carbon is shown in Figure 5, where a gas-chromatrogram of an extract of a loaded activated carbon from a waterworks filter is shown.

Fig. 5: Gas-chromatogram of an activated carbon extract

This figure, which is representative of many similar results, shows why adsorption techniques have become of such increasing importance. Many of the identified compounds which were removed in the activated carbon filter mentioned above are undesirable in drinking water. Only activated carbon filters are able to achieve the degree of removal required, at present.

When discussing organo-chloro compounds, it is necessary to remember that when waters with a high concentration of organics are chlorinated, organo-chloro compounds are also produced (ROOK 1974). As Figure 6 shows, fairly high concentrations of organo-chloro compounds can be observed (SYMONS 1975).

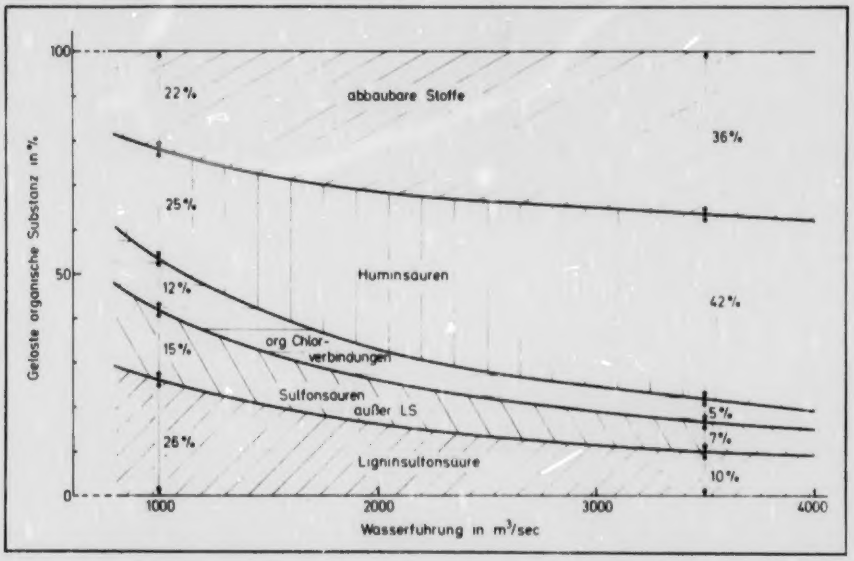

Fig. 4:

Gelöste organische Substanz in %: dissolved organics in per cent
abbaubare Stoffe: degradable substances
Huminsäure: humic acids
org. Chlorverbindungen: organo-chloro compounds
Sulfonsäuren außer LS: sulphonic acids except LS
Ligninsulfonsäure: lignin sulphonic acid (LS)
Wasserführung in m^3/sec: flow rate in m^3/sec

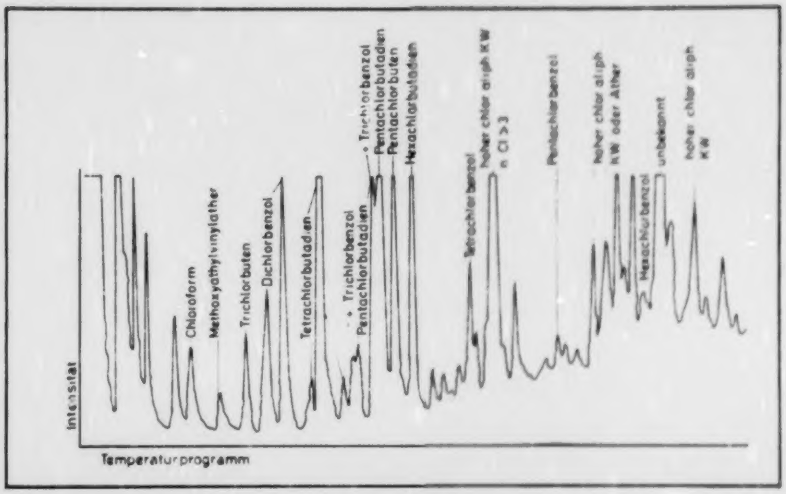

Fig. 5:
Intensität: intensity
unbekannt: unknown

Fig. 6: Frequency distribution of different trihalogen methanes in chlorinated USA drinking waters (SYMONS)

According to the data in Figure 6, chloroform concentrations of up to 0.1 mg/l have been measured. Furthermore, there is a relationship between the concentration of dissolved organic carbon in the treated water and the concentration of organo-chloro compounds (see Fig. 7). This topic is of special importance.

Fig. 7: Dependence of the medium concentration of trihalomethane compounds on the concentration of dissolved carbon (SYMONS)

Although taking into consideration the relatively high chlorine dosages used in the USA, it may be deduced from these results that it is not only important to remove the existing organo-chloro compounds from the raw water during drinking water treatment but that one should also lower the total concentration of organic materials. Otherwise, organo-chloro compounds will be produced during chlorination, which is necessary for disinfection before distribution.

However, it should be mentioned too that dissolved organics, especially fulvic acids, act as corrosion inhibitors (SONTHEIMER 1969, RUDEK 1975). Therefore, it is not advisable to remove too much of these organic substances.

Considering that all raw waters contain a great amount of different substances and that competitive and selective adsorption may cause an increase in the concentration of certain compounds - as can be seen from gas- or liquid chromatography analyses - it becomes clear how difficult it is to produce a common evaluation for the adsorbent quality and the running time of an activated carbon filter. Additional difficulties arise due to the different operation conditions at each waterworks. In addition, process and technological points of view, as well as security in treatment effectiveness with changing water quality, have to be considered.

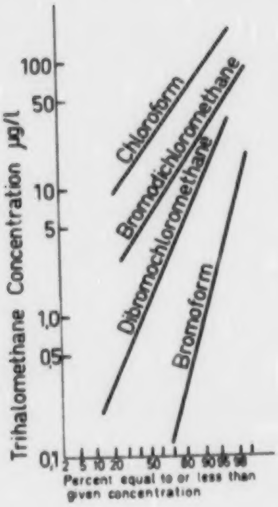

Figure 6

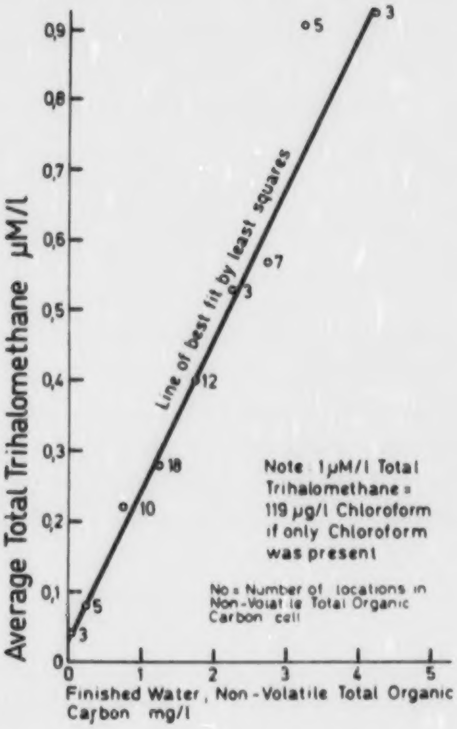

Figure 7

To sum up all these aspects for the control of adsorption processes - despite all the difficulties - the following recommendations, set out in Table 1, can be made:

Table 1: Recommendations for controlling adsorption processes (activated carbon filters) for drinking water treatment

1) Evaluation of activated carbon with several parameters
    a) Examination of adsorption equilibria for adsorptive mixtures;
    b) Selection of adsorptive mixtures in respect of the practical problems;
    c) Examination of adsorption kinetics.
2) Evaluation of running time with different parameters
    a) Reduction of UV extinction;
    b) Loading with non-polar and polar organo-chloro compounds at different filter layers;
    c) Removal of odour substances;
    d) Measurement of biological effectiveness;
    e) Comparison with laboratory testing methods.
3) Periodic control of the effectiveness of the activated carbon filters
4) Coordination of the additional treatment steps with the effectiveness of the activated carbon filters

Because more detailed explanations are made on the topics mentioned above in other papers, only some general remarks are made here. From the experience available to date, it can definitely be concluded that parameters such as phenol loading or phenol value, iodine number etc., give no relevant information for the evaluation of activated carbon used in waterworks. Here the displacement of adsorbed material caused by competitive adsorption is nearly always of such importance that only measurements of the adsorption equilibria with mixtures of substances, which show some correlation with the pratical problem, are worthwhile carrying out. Furthermore, in addition to the adsorption equilibria - to avoid misinterpretation - kinetic studies are always necessary.

Similar aspects have to be considered for the regular control of the carbon filters. Although the control of the reduction in UV extinction is easy and useful, and although these results correlate well with other sum parameters such as DOC, this value alone provides little information about the effectiveness of an activated carbon filter.

On the one hand, it can be concluded that an extensive removal of organics would inevitably result in the removal of all undesired and hazardous material.-However, according to results available so far, this is only valid when more than 80 per cent of the total dissolved organics are removed. - On the other hand, such a high degree of removal is not always required. It is therefore necessary to carry out additional investigations on the loading of activated carbon with organo-chloro compounds and also on the removal of taste and odour, together with investigations on the biological effectiveness of the filters. The results obtained from the large filters should also be compared with the laboratory tests.

If such a control of the filters is carried out regularly, and the other treatment steps are optimized at the same time, the necessary informations will be obtained for each individual case to decide on the running time before regeneration, the choice of the proper carbon quality and on the optimum process data.

It is quite possible that this kind of procedure will lead to different conclusions on the optimum running conditions in activated carbon plants at different waterworks. Nevertheless, important conclusions on the optimum application of adsorption techniques can be drawn from the experiences at different places. Therefore, the results obtained at different waterworks are discussed in detail in a number of the following papers.

However, experience alone, without an understanding of the process itself, may lead to misinterpretations. Therefore, reports of practical work are supplemented by papers dealing with basic aspects of these processes. The research work for these was supported by grants given by the Federal Ministry of Research and Technology in a programme called "New technologies of water treatment" and by the German Research Association in the Special Research Group 62 entitled "Basic processes in water and gas purification". In addition, the research work carried out at the Engler-Bunte-Institut was supported by different German waterworks.

This support deserves recognition and appreciation, as do the intensive activities of the waterworks in solving their own problems in the use of activated carbon filters. This shows the importance of adsorption techniques in the field of drinking water, where they are indispensable in solving many problems on quality control.

16

MANUFACTURE AND PROPERTIES OF ACTIVATED CARBON

by

H. Jüntgen, Essen

1. Introduction

An adsorbent consisting mainly of carbon having a distinct structure of pores is called activated carbon. The general scheme of the highly ramified pore system is shown in Fig. 1 .

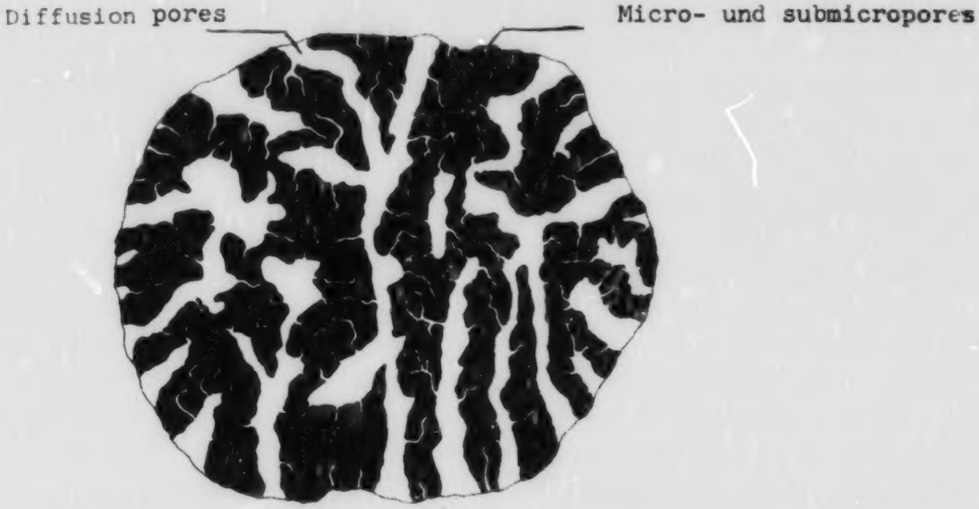

Fig. 1: Scheme of the pore structure of activated carbon

The particle of activated carbon as shown on Fig. 1 exhibits macropores of a diameter ≥ 500 AE (Angstrom) which extend all through it. The transport of the adsorptives from the outer particle limit to the pore system is effected rapidly; thus, these macropores are also called "admission pores" or "diffusion pores". From these macropores numerous finely ramified meso-, micro- und submicropores branch off, the diameters of which are < 500, < 2o and < 8 AE respectively. Since for cylindrical or irregularly shaped pores the wall surface increases considerably with decreasing diameter, the walls of the micro- und submicropore systems constitute the majority of the activated carbon's inner surface. This inner surface may amount from 5oo up to 1 5oo m^2/g of activated carbon and can thus bind a large number of adsorptive molecules. Considering that the surface requirement of one millimol of a normal organic substance amounts from loo up to looo m^2 at weights of 7o to 5oo mg, the load of a medium-quality activated carbon at full saturation of the surface may be estimated to be 5o to 7o % (by weight) of organic matter.

As a characteristic feature for the carbon structure of activated carbon the adsorption heat at adsorption of non-polar organic matter is considerably higher than the one of adsorption of polar-organic matter or of water. This behaviour, also called hydrophobia, means that in contrast to other adsorbents activated carbon adsorbs selectively the non-polar organic matters. Due to its hydrophobic surface activated carbon is especially suitable to adsorb organic pollutents contained in low concentration in waste waters of all kind. Since recently the use of grain-sized activated carbon became more and more widespread for those purposes, the present note shall deal exclusively with the manufacture of grain-sized activated carbon. A detailed descriptio of all manufacturing processes has been set up by W. Aehnelt (Ullmanns Encyklopädie der technischen Chemie, 3. Auflage, Bd. 9, S. 8oo).

Basic principles for the manufacture of activated carbon

The manufacturing principle consists in selective removal of certain components of suitable carbon-containing material by a subtraction without shrinkage of the grain so that defined hollow spaces remain instead of the removed components. The most simple process,applied since more than 2oo years consists in the pyrolysis of wood or other organic material. In the course of this pyrolysis volatile matter is removed and the remaining carbon-containing residue exhibits already a certain porosity. The pyrolysis of organic matter consisting of carbon hydrates or cellulose can be controlled by use of water-separating additives as e.g. zinc chloride or phosphoric acide in a way that a considerably greater pore system is obtained than in case of a pyrolysis without use of such additives. The method described is also referred to as "chemical activation". The pore system of a pyrolysis residue - sometimes also called "coke" - may in many cases be systematically enlarged and modified by reaction of a coke at higher temperature with oxidation agents as e.g. steam or CO_2 which transfer selectively a part of the carbon substance into the gaseous phase thus leaving hollow spaces. Table 1 shows a selection of carbon-containing raw materials, predominantly used nowadays for manufacture of activated carbon by means of chemical activation and gas activation processes. Whereas the chemical activation process is confined to cellulose-containing raw materials - here called wood - the number of raw material for the gas activation process is considerably greater and ranges from wood and peat to hard coal and petroleum coke.

Process	Raw material	Activation agent
Chemical activation	Wood	$ZnCl_2$, H_3PO_4 etc.
Gas activation	Wood Peat Lignite Hard coal Petroleum coke	H_2O_D CO_2

Table 1: Manufacture of activated carbon - Process and raw materials

Before activation, the basic material used for activated carbon production has to be brought to uniform size. Several methods are available for this purpose which are shown on Table 2. By extrusion of a blend of fine basic material and binder, several very solid cylindrically shaped pieces with a smooth surface can be obtained in a range of graine size between 1 and 9 mm. The grains are fairly uniform in size.

Generally, the diameter of the cylinder varies only within very tight tolerances, whereas the length of the individually shaped particles is somewhat non-uniform. By this process, also particles of a length equal to their diameter can be produced. Pelletisation constitutes another method of shaping. By this method ball-shaped particles of satisfactory hardness are obtained, however, the range of sizes is considerably greater than for extrusion products. For adsorption purposes, pellets of 4 to 9 mm in size may be produced. Another method for shaping small-particle basic material consists in agglomateration with subsequent crushing and screening which can be carried out after pyrolysis or after activation. Due to the crushing, the shaping of individual particles is irregular and the surface of the particles is rough. The hardness of these particles may be good or even very good . The range of grain sizes is wide. Eventually, also basic material of natural granularity may be used for manufacture of activated carbon in the course of which it is crushed either before or after activation. Also in that case the particles are of irregular shape and rough surface, but the hardness is generally inferior to the one of the products obtained by the shaping processes (H. Dratwa, H. Jüntgen, Staub-Reinhaltung der Luft, 27 (1967), p. 3o1/3o7).

Shaping	Grain size	Range of sizes	Grain shape	Grain surface	Hardness
Extrusion	1 - 9	narrow	cylindrical	smooth	very good
Pelletisation	4 - 9	wide	round	nearly smooth	satisfactory
Agglomeration and crushing	o -1o	wide	irregular	rough	very good to good
Crushing	o -1o	wide	irregular	rough	satisfactory

Table 2: Manufacture of activated carbon - Shaping process

Description of chemical activation process

On Figure 2 a schematic representation of the individual process phases for chemical activation of activated carbon is shown (M. Smisek and S. Cerny, Active Carbon, Elsevier Pub., Amsterdam (197o)). The raw material is first ground to fine grain size and then blended to a certain ratio with an activation reagent, e.g.

zinc chloride or phosphoric acid. The paste thus obtained is then brought to shape by the processes described in the previous chapter, extrusion being preferred. After shaping the products obtained must be dried according to a clearly defined process. Then, calcination is carried out in rotary kilns at temperatures ranging from 7oo to 9oo °C, the activation agent being partly removed by distillation and subsequently recovered. After cooling a wet extraction is carried out in order to remove the quantity of activation agents still contained in the pore system. Again, the removed residual activation agent is recovered from the aqueous solution. After chemical activation wet treatment with steam at 5oo °C may be practised in order to make the surface hydrophobic.

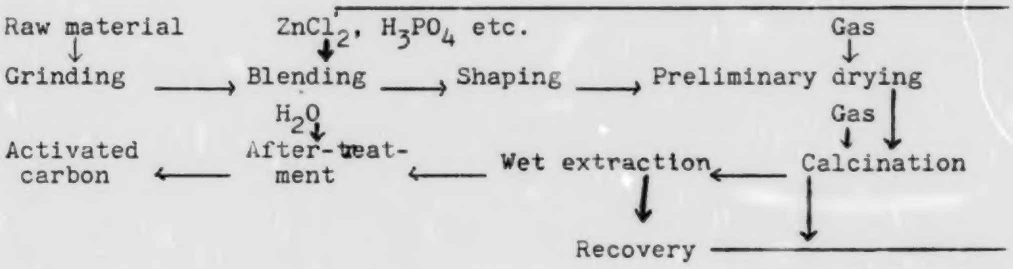

Figure 2: Manufacture of activated carbon - chemical activation -

Process description of gas activation of activated carbon

Figure 3 gives a schematic view on the process phases for gas activation (H. Jüntgen, Ber. Bunsenges. Phys.Chem. 1975). In this case, too, the raw material is ground to fine granular sizes and, if necessary, subjected to preliminary treatment. In case of e.g. hardcoal used as raw material this preliminary treatment consists of an oxidation in atmospheric air at temperatures below 3oo °C. After this pre-treatment the fine dust is blended with binder and brought to cylindrical shape. The shaped products are subjected to pyrolysis at temperatures between 6oo and 9oo °C in ambiance of inert gas. During this pyrolysis a residue is produced which subsequently is treated at temperatures between 7oo and 9oo °C with oxidizing agents, as e.g. steam or CO_2.

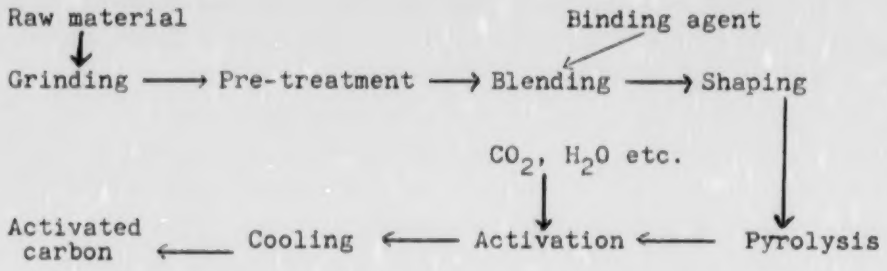

Figure 3: Manufacture of activated carbon - Gas activation -

The steam reaction or Boudouard reaction, respectively, which takes place has been examined very carefully under various points of view. Especially the mechanism and the kinetics of these reactions are well known (K. Hedden, Ullmanns Encyklopädie der technischen Chemie, 3. edition, Vol. 10, p. 362). Due to this knowledge the reaction can be controlled so that a well-defined pore system can be obtained. After activation the product is cooled and packed.

Properties of activated carbon obtained by gas activation

The properties of activated carbons depend in a fairly complex manner on the raw material used and on the activation process applied. Within the framework of the present note a comprehensive view on this cannot be given. Therefore, some observations pertaining to the properties of gas-activated carbons in function of different parameters of the manufacturing process shall be quoted as examples.

Detailed investigations carried out by Bergbau-Forschung have shown that the macropore system of activated carbon is pre-determined already during the shaping process and definitely fixed by the subsequent pyrolysis (H. Jüntgen's inaugural dissertation)*). It is easily imaginable that during extrusion the original void volume between the individual grains of carbon is filled up by the binder, the individual grains being agglomerated under the pressure applied. During the subsequent pyrolysis mostly macropores are created in the void volume filled up by the binder, by disintegration of the latter, since the coke residue of the binder is comparably small. It is, therefore, to be expected that the macropore volume of the formed grains depends not only on the forming pressure but also on the grain size and grain distribution of the carbon dust used, since the latter data have a decisive influence on the void volume. For illustration Fig. 4 shows the integral pore distribution of the macropore system - measured by mercury porosimetry - within shaped products immediately after pyrolysis, three carbon-containing raw material qualities of different grain size having been used. A material containing a relatively high proportion of coarse grains and a very heterogeneous grain distribution results in a macropore system with a range of pore radii from lo^4 to lo^6 AE. This range is obviously very wide. When using a feed stock containing a smaller share of coarse grains, this range may be kept narrower and the most frequent pore radii are lo^4 to lo^5 AE. Furthermore, the total volume of macropores is reduced. A very fine dust with a relatively narrow grain size distribution eventually results in a macropore system with a very narrow range of radii, mostly of approx. lo^4 AE. Again, the total volume of macropores is further decreased.

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*) Heidelberg, 1966

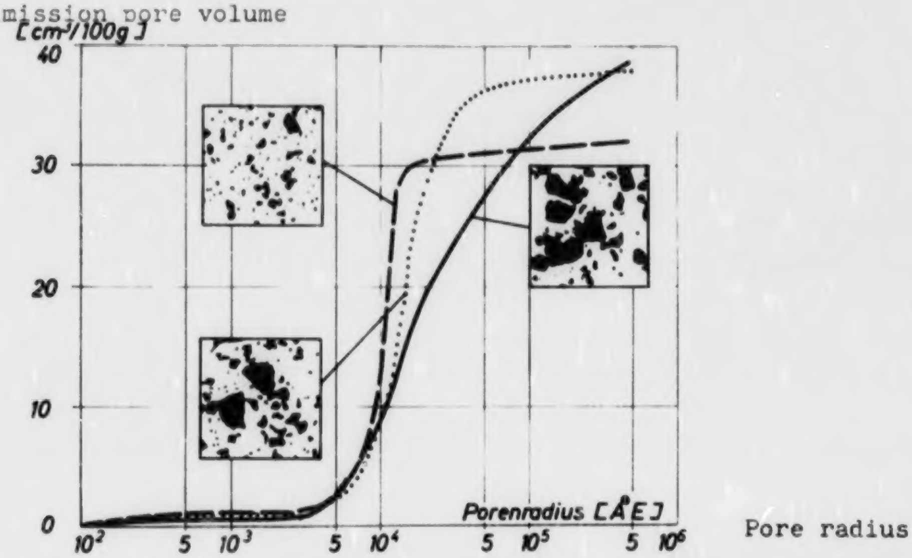


Fig. 4 Manufacture of activated carbon - Influence of grain size

The control of the activation process is of particularly decisive influence on the micropore system and, thus, on the properties of the activated carbon. In case of very short treatment periods in activating gas atmosphere only a small share of the carbon is partly gasified and, consequently, the micropore system obtained is small. With increasing activation time the micropore system may purposely be increased. The degree of activation may preferably be defined by the recorded portion of the carbon originally contained which partly gasified by the activation process. Fig. 5 shows the most important properties of activated carbon in function of the degree of activation represented schematically in the abscissa. First, it is noted that the bulk density decreases nearly linearly with increasing degree of activation. The decrease of bulk density is due to the pore system becoming larger with increasing degree of activation, i.e. due to the decreasing apparent density and the constant real density of the material. The development of the micropore volume is different from the one of the macropore volume. These developments are not related to grams of activated carbon but to loo ml bulk volume of activated carbon. The micropore volume increases nearly linearly with increasing degree of combustion. This strong increase may be explained by the gasification reaction taking place predominantly on the total inner surface of the coke and, thus, forms mostly very fine micropores.The macropore volume increases relatively moderately in the course of activation. Furthermore, it was found - not illustrated here - that the pore distribution of the macropore volume is not significantly influenced by the activation process.

In Fig. 5 it is shown that the average adsorption pore diameter increases sharply with increasing activation, viz. by the factor 2.5, i.e. with increasing activation activated carbon becomes increasingly wide-pored. As expected, the inner surface does not increase uniformly over the whole activation process. It is even to be noted that after a sharp increase and a maximum period a slight decrease follows. The reason is that at the

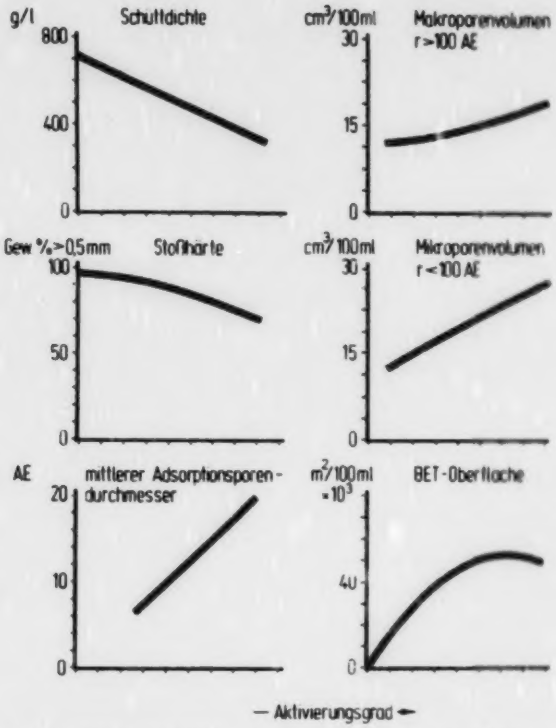


Fig. 5 Manufacture of activated carbon - Influence of the degree of activation -

Schüttdichte = bulk density
Makroporenvolumen = macropore volume
Stoffhärte = impact hardness
Gew.-% = % (by weight)
Mikroporenvolumen = micropore volume
Mittl. Adsorptionsporendurchmesser = average adsorption pore diameter
BET Oberfläche = surface as per BET
Aktivierungsgrad = degree of activation

beginning of activation mostly narrow pores are formed, the surface of which contributes largely to the total inner surface. Later on, activation predominantly causes a growth of the smaller pores so that the increase of the specific inner surface is slowed down and later on even turns into decrease. With increasing micropore volume and macropore volume the carbon structure necessarily becomes more fragile, i.e. the so-called impact hardness decreases, firstly fairly slightly, however more pronounced beyond the medium values of degree of activation. The changes in pore distribution within the micropore volume are shown on Fig. 6. Here, the differential pore distribution of activated carbon with different degree of activation values is shown. The respective values have been established by measuring benzene adsorption and subsequent assessment according to Dubinin-Radushkevich using Thomson's equation (H. Jüntgen, H. Seewald, Ber. Bunsenges. Phys.Chem., 1975). The differential pore volume dV/dR is plotted against the pore radius.

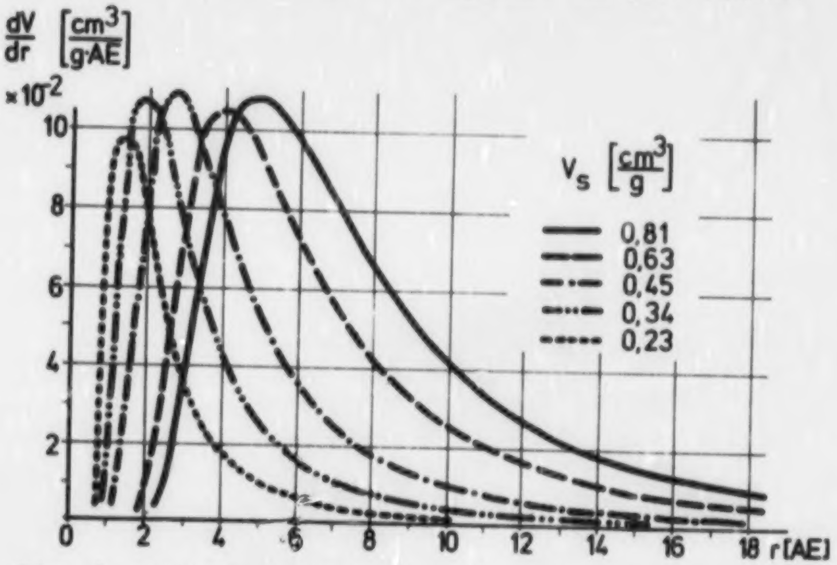


Fig. 6 Volume distribution of adsorption pore system of different activated carbon qualities

From these curves the average pore radii, i.e. the average pore diameters shown in Fig. 5 are determined by separating the surfaces under the curves into two equal shares. From the graphical representation it may be noted that with increasing degree of activation the pore volume - integral below the total curve - as well as the most frequent and the average pore radius - increases. The average pore radius is approx. twice as large as the most frequent one. The micropore distribution depends not only on the degree of activation but also on the raw material. This fact may be exemplified by Fig. 7 showing the differential pore distributions of two activated carbon qualities exhibiting the same degree of activation, but being made from different raw materials. Also in this way the pore distribution can be considerably influenced. Thus, both curves shown exhibit a ratio of 1:2 when comparing the most frequent pore radii.

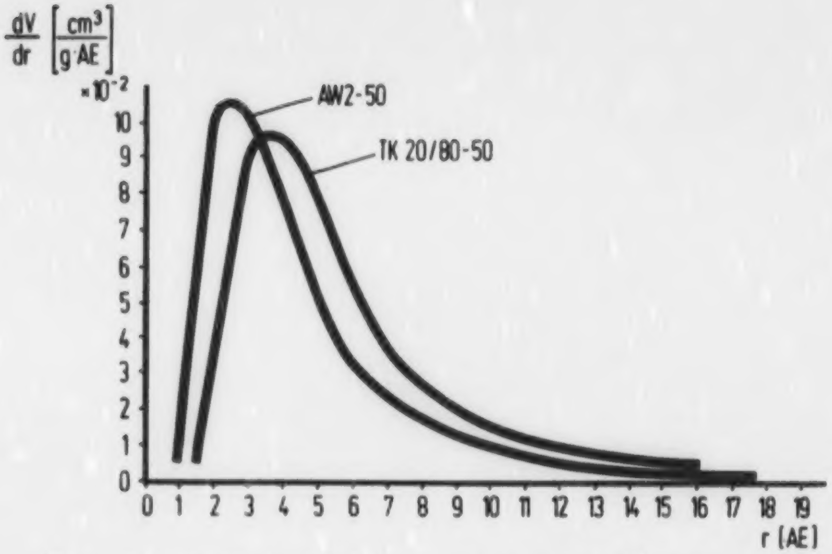


Fig. 7 Differential pore radii distribution of activated carbon

Even though the specialist may draw certain conclusions from the properties discussed - pore volume and pore distribution - the requirement for thorough examination continues to exist for the assessment of the applicability of activated carbon coming from different manufacturing processes. This point of view is so complex that it should not be discussed within the framework of the present lecture. Nevertheless, it should perhaps be pointed out that the adsorption of organic matter from aqueous solutions also depends on the relation of molecule size to micropore diameter In Fig. 8 the adsorption of different organic matter from an aqueous phase is plotted against activated carbon qualities of different degree of activation, based on a residual concentration of 5o mg/l. These organic matters are different by their molecular weight. In particular, these matters are: phenol (molecular weight 94), Na-salt of p-n-dezylbenzenesulfanate (molecular weight 32o) and p-n-nonylphenolnonaglykolether (molecular weight 612). It is to be noted that the phenol adsorption first increases with increasing degree of activation, then passes through a maximum and subsequently decreases, whereas the adsorption of the two other materials is completely insufficient at small degree of activation. however sharply increases with increasing degree of activation and eventually is higher than the phenol adsorption at high degree of activation. A detailed explanation for this complex behaviour cannot be given within the framework of the present lecture.

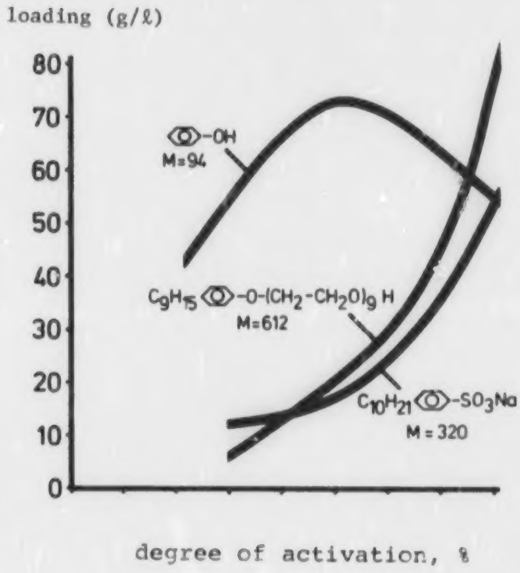


Fig. 8 Characterization of adsorption capacity in aqueous solution

The ratio molecular diameter/pore diameter is one of the essential features: whereas phenol adsorption at medium degree of activation seems optimum, the high-molecular materials are only adsorbed satisfactorily by wide-pored activated carbon, the difference between the two high-molecular materials mentioned before being not too significant. The last-mentioned fact may be due to the oblong molecular shape, the steric behaviour of which may be comparable in case of diffusion in relatively narrow pores. Of course, in this context, the polar character and the solubility of the materials may be of certain importance for the adsorption behaviour. This example may, however, show that it is impossible to find an activated carbon quality which exhibits optimum adsorption properties for all materials. Thus, it is obviously necessary to adapt the activated carbon quality to the specific adsorption problems.

6. Conclusions

This more general lecture is supposed to discuss only some essential points of view for activated carbon production. It was intended to show that by choice of activation process of the feed stock and by the adjustment of certain activation conditions the properties of activated carbon may be changed nearly at will. Thus, it will always be possible to make activated carbon with optimum properties for specific application on the basis of appropriate development work.

BASIC PRINCIPLES OF ADSORPTION PROCESS TECHNIQUES

by H. Sontheimer

Introduction

During adsorption, organic molecules are removed from the water by being attached at the large inner surface of the adsorbent which, in the case of activated carbon, may be as large as 1000 m^2/g. To describe the adsorption process mathematically, which is necessary to design adsorption plants, knowledge of the adsorption kinetics and adsorption equilibrium is required. The literature references at the end of this book give a survey of some of the most important work in this field.

Although many investigations and theoretical calculations have been made in order to describe the adsorption equilibrium and the kinetics, the design and optimization of adsorption plants in waterworks still have to be made empirically in most cases. This is mainly due to the following:

1) Activated carbon used for water purification is nearly always made from natural products and can be characterized by empirical data only. This makes it difficult to describe activated carbon qualities and the processes taking place during adsorption.

2) The raw water always contains a large number of organic substances which interfere with each other during adsorption.

The complex nature of these problems makes it difficult to design an adsorption plant for water treatment. Nevertheless, knowledge of the unit operations used by adsorption techniques, as given in Vol. 8 of the Engler-Bunte-Institut series, provides a valuable guide on the effective application of adsorption processes in drinking-water treatment. This paper is intended, in the main, to take a more detailed look at these relationships, based on the knowledge of the adsorption behaviour of single substances.

Adsorption equilibria

In an aqueous solution of organic substances, the adsorption isotherm describes the final state of the adsorption process. The loading q of the activated carbon is specified in g or mol of organic substance per kg of activated carbon as a function of the residual concentration c in g/m^3 or mol/m^3. The Langmuir isotherm, one of the best known relations for the description of the adsorption equilibria, is shown in Fig. 1.

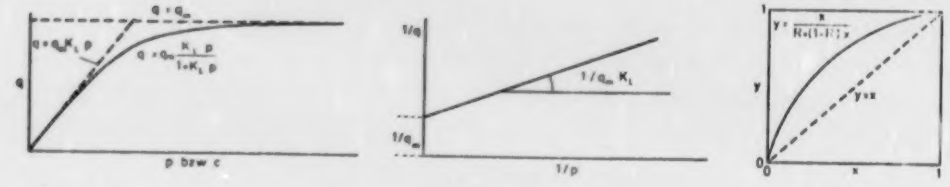
Fig. 1: Langmuir isotherm

The Langmuir isotherm can be deduced from a simple mathematical model. A characteristic of this isotherm is the fact that the loading of the carbon approaches a limiting value q_m as the concentration increases, corresponding to a monomolecular coverage of the surface.

The two parameters of the Langmuir isotherm can be determined from the measured adsorption equilibria. A linearization of the relationship can be obtained by plotting the reciprocal values of q and c (Engler-Bunte-Institut, Vol.8,1975). When c is related to c_o, the initial concentration, a dimensionless representation is also possible. Using this method of description, there is only one parameter R, the separation factor. If R is < 1, as is the case in Fig. 1, then one speaks of a favourable equilibrium. If the curve lies below the y = x line, then R is > 1 and the equilibrium is said to be unfavourable.

However, whereas the Langmuir isotherm can only be applied in rare cases for adsorption from the aqueous phase, the Freundlich adsorption isotherm provides in most instances a better description of the adsorption equilibrium, as shown in Fig. 2 FRITZ 1975).

Fig. 2: Adsorption isotherms of p-nitrophenol (1) and phenol (2)
Comparison: Langmuir-Freundlich-isotherms



a) normal b) linearisiert c) dimensionslos

Fig. 1
linearisiert: linearized
dimensionslos: dimensionless

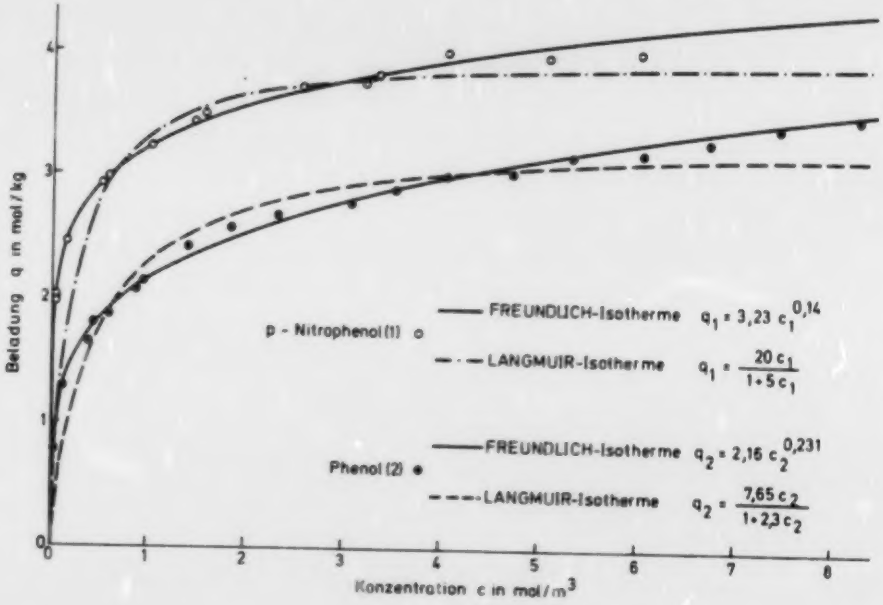
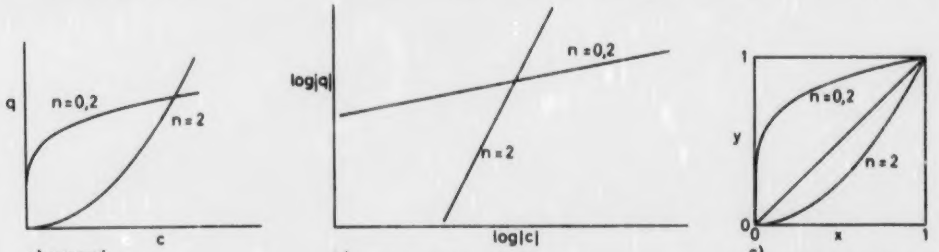


Fig. 2: Beladung q in mol/kg: loading q in mol/kg

Here the adsorption of phenol and p-nitrophenol onto an activated carbon, B 10, are described using Langmuir and Freundlich isotherms. One can easily see the better fit of the values obtained using the Freundlich isotherm. A plotting of this isotherm, its linearization, using a double logarithmic plotting, and the corresponding dimensionless representation are shown in Fig. 3.



a) normal b) linearized c) dimensionless

Fig. 3: Freundlich isotherms

In Fig. 3 two representative isotherms are shown which describe completely different adsorption behaviours. They are referred to (Fig. 3 b) as flat (n = 0.2) and steep (n = 2) isotherms. When considering the behaviour of activated carbon filters, it is important to remember that gradients greater than 1 (n = > 1) lead to an unfavourable equilibrium. Under such circumstances one can expect that the complete removal of the substances in a filter will be difficult to obtain. Such isotherms are found fairly frequently in drinking water treatment, for instance with humic acids.

In contrast, gradients less than 1 (n = < 1) are nearly always obtained for defined single substances, as for instance nonpolar organo-chloro compounds. Due to the favourable equilibrium, such substances can nearly always be easily removed with a carbon filter.

It is important for all practical considerations to bear in mind that the Freundlich isotherm describes the adsorption behaviour only over a limited concentration range, so that every investigation of adsorption equilibria should be made in the concentration range for which the activated carbon treatment is intended. Investigations at higher concentrations, which are often made because of the greater accuracy of measurement, cannot therefore be transferred directly to other concentration ranges. This applies even to pure substances, as can be seen in Fig. 4 for p-nitrophenol and phenol isotherms (FRITZ 1975).

Fig. 4: Freundlich isotherms of p-nitrophenol and phenol over a wide concentration range

The illustrated equations for the various ranges show that the isotherms increase in gradient at lower concentrations, with a corresponding increase in the two constants K_F and n.

Data can be correlated over a wide range, using a single relationship such as that of RADKE and PRAUSNITZ (1972); however, a third parameter is then necessary. Because of this complication such an equation is therefore seldom used. It is only mentioned here for the sake of completeness and because it has the advantage that it can be applied in most cases of practical interest in adsorption from liquids since it includes as limiting cases the pure Langmuir and Freundlich isotherms (FRITZ 1974). The application of the Freundlich isotherm has the advantage in practical problems in water treatment that group parameters such as DOC or UV extinction can be used for the determination of an isotherm, and that nearly always reasonable straight line double logarithmic plots are obtained. Even adsorption isotherms where only odour threshold numbers are used instead of concentrations can be described in this way, as shown in Fig. 5 (Engler-Bunte-Institut, Vol. 2, 1967).

Fig. 5: Adsorption tests with water from the Lake of Constance (sampling station Sipplingen)

One can see quite well from this illustration that, despite the difficulties to obtain exact measurements of odour threshold numbers, they can be quite well described by a Freundlich isotherm.

However, it is also obvious that the isotherm gradients may differ widely and that values greater than 1 are possible. This indicates, however, as already mentioned, that a complete removal of the particular material is difficult to obtain. Nevertheless, attention must be paid not only to the slope of the gradient but to the position of the isotherm. The description of the adsorption equilibrium becomes even

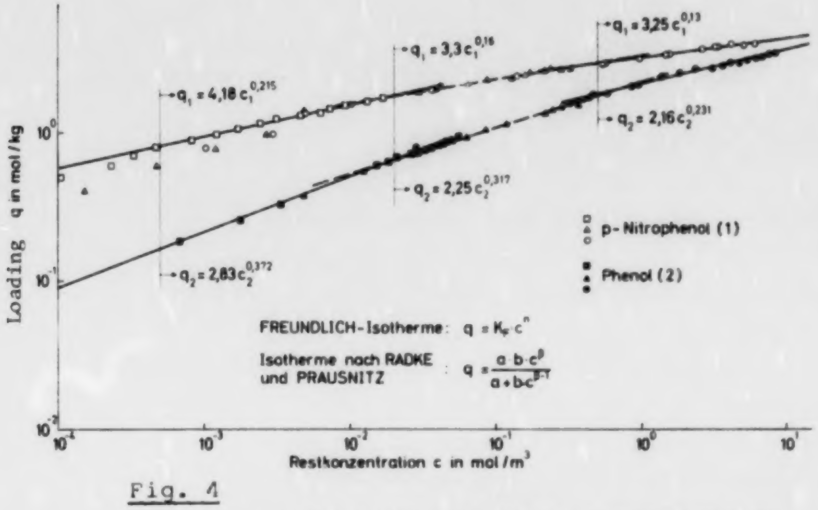
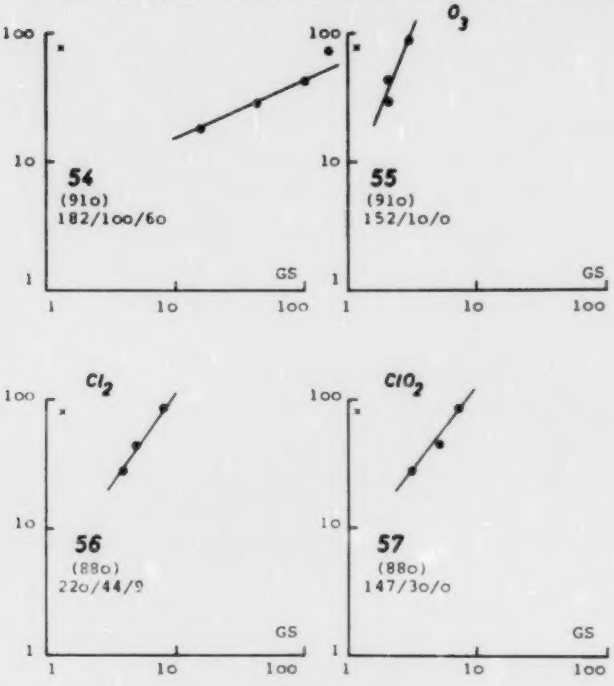


Fig. 4

Restkonzentration: residual concentration



Verwendete Aktivkohle: Hydraffin 104

Abszisse: Geruchsschwelle GS

Ordinate: Beladung × = $[(GS_0/V) - GS]/a$

runde Klammer: GS_0/V

Fig. 5

Verwendete Aktivkohle: Type of carbon used

Geruchsschwelle: odour threshold

runde Klammer: round brackets

more complicated when several organic substances are present in the solution. This can be seen especially well with the combination phenol - p-nitrophenol. The measured adsorption isotherms for this system are shown in Fig. 6 (FRITZ 1974).

Fig. 6: Adsorption isotherms, at 20 °C, of p-nitrophenol (1) and phenol (2) on B 10

In the upper part of this figure the isotherms for p-nitrophenol are plotted in the presence of different amounts of phenol; it may be seen that this has little influence on the adsorption of p-nitrophenol. In contrast, as may be seen in the lower part of this figure, the presence of p-nitrophenol has a strong influence on the adsorption of phenol. According to these measurements, p-nitrophenol is very much better adsorbed than phenol and displaces it from the activated carbon.

In this case the different solubilities of the two substances play an important role, as may be seen in Fig. 7 (BALDAUF 1975).

Fig. 7: Isotherms of phenol and p-nitrophenol with different methods of plotting

In the upper part of this figure the normal isotherms are plotted, whilst in the lower part the results are plotted with the ratio residual concentration to saturation concentration (solubility) as abscissa.

With this type of presentation the two isotherms practically coincide because phenol is much more soluble than p-nitrophenol. This difference also explains to a great extent the behaviour of both substances during mixed adsorption.

However, this is not always the case, as can be seen in Fig. 8, where adsorption data of the mixture benzoic acid - p-nitrophenol are shown (FRITZ 1975).

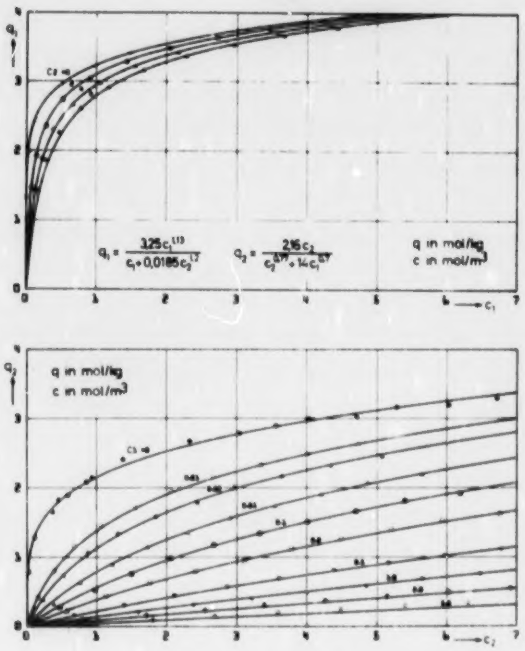


Figure 6

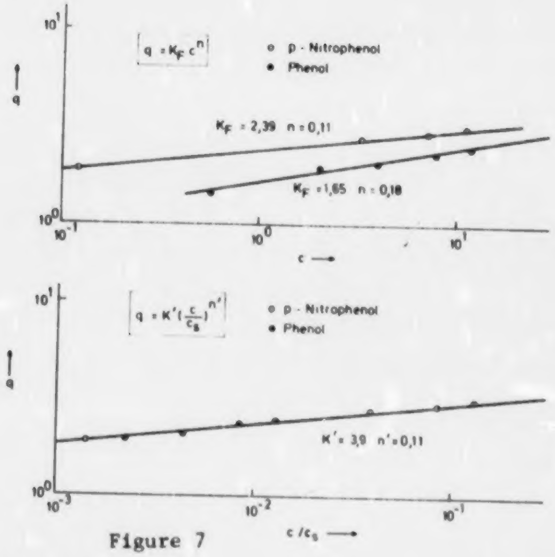


Figure 7

Fig. 8: Adsorption isotherms, 20 °C, for p-nitrophenol (1) and benzoic acid (2) on B 10

Here, the two substances displace one another almost equally strongly, despite large differences in solubility. From this and other results it can be deduced that for the mutual displacement on the carbon and the resulting hindrance of the adsorption of a substance chemical parameters are also important, in addition to the solubility.

The behaviour of adsorption mixtures can be well described by an empirical equation, provided the individual substances have Freundlich isotherms (FRITZ 1974). The relations deduced from some adsorption mixtures can be used to predict how two different adsorbents behave during combined adsorption. From these calculations one comes to the conclusion, in a number of cases involving mixtures, that better results can be obtained with a suitable choice of adsorbents than when each is adsorbed alone, as is shown in Fig. 9 (BALDAUF 1975).

Fig. 9: Calculated adsorption isotherms

It can be seen that, at least theoretically, better results can be obtained with mixtures of adsorbents than with individual adsorbents.

Fig. 10: Break-through curves in large filters with different types of activated carbon (RWW Mülheim)

That such considerations can also have practical consequences is shown in Fig. 10 (VOLLMER, NOLTE 1974), in which break-through curves for a large filter are shown with three different types of carbon. Also included is a break-through curve for a mixture of equal quantities of two carbons. Better results were obtained in the first month of running time with the mixed carbons than with the two individual carbons, especially

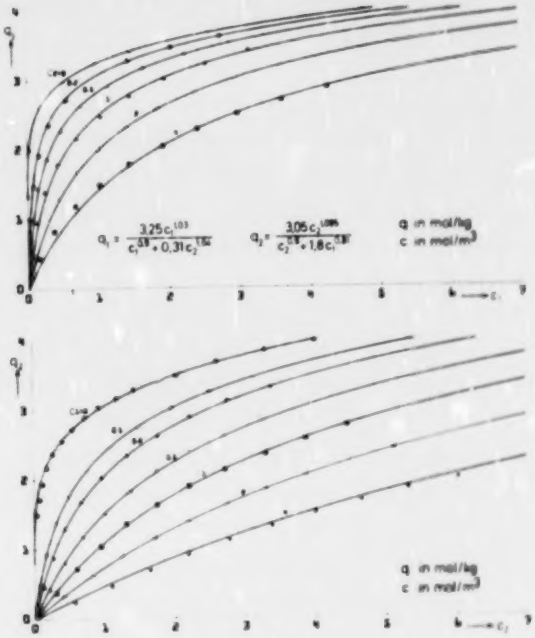


Figure 8

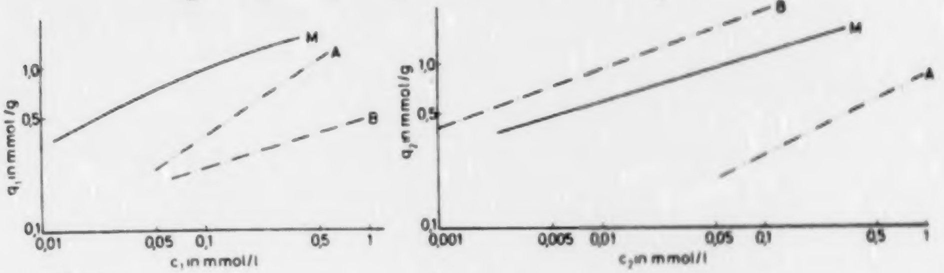


Figure 9

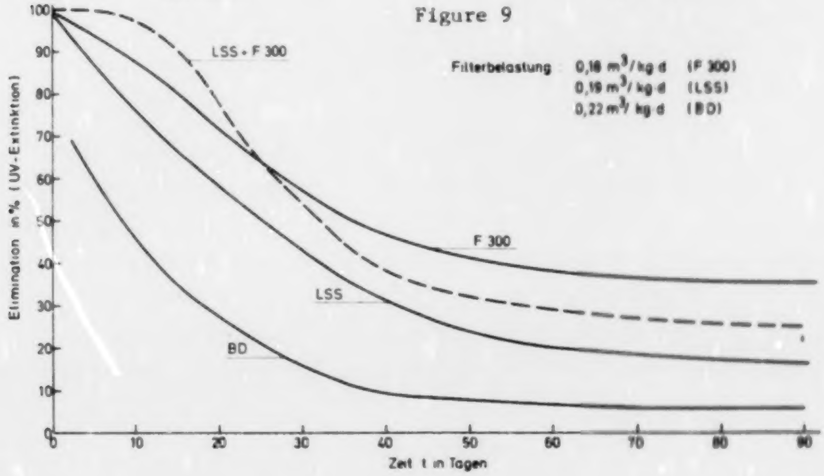


Fig. 10

Filterbelastung: filter loading

Zeit in Tagen: time t in days

in the case of organo-chloro loading. Although the effect is not very pronounced, considering the total filter running time, it is nevertheless quite interesting and may be worthwhile pursuing further. In this connection, adsorption kinetics also play an important part. Before examining this in further detail, it is advisable to point out the consequences of adsorption equilibria which are important in practice. They are summarized in Table 1.

Table 1: Practical significance of adsorption equilibria measurements

1) Evaluation of results using the Freundlich isotherm (double logarithmic plotting)

$$q = K_F \cdot c^n$$

Important numerical values:

a) $q = q_o$ for $c = c_o$

A high q_o leads to a high loading in the filter.

b) n = adsorption exponent (slope of the double logarithmic plot)

Precondition for an efficient removal of organic substances in the filter: $n < 1$.

2) Carbon evaluation, because of competitive adsorption only using adsorptive mixtures

3) Use of adsorbent mixtures

Prediction of the suitability by isotherm measurements.

The table shows that it is important for the practical evaluation of carbons that the values for q_o and n are determined from experimentally measured isotherm data, because these numerical values provide a direct indication of the behaviour of the carbon in the filter. It is therefore advisable to always determine these two numerical values from equilibrium measurements.

Also of great importance is to note the behaviour of the competing adsorption for the evaluation of the effectiveness of certain types of activated carbon. Although this reduces the choice of suitable test methods quite considerably, it is, according to current experience, absolutely essential.

Such measurements can also provide an indication of the possible advantage of using adsorbent mixtures. The advantages of such a method of operation are only small because of the activated carbon qualities on the market at the moment, but the advantages of a flocculation prior to adsorption, reported by HEYMANN and SCHEIDTMANN (1975) show clearly that all the optimization possibilities have not been utilized by any means yet.

That this is often not possible must be put down to strongly differing adsorption kinetics of the various carbon types, which are discussed in more detail in the following chapters.

Adsorption kinetics

A mathematical description of the adsorption kinetics requires as a prerequisite a suitable model of the process and the rate-determining mechanisms (HEIL 1971). However, the difficulties involved in producing a general description become apparent when one examines electron-micrographs of different types of carbon, remembering that the pore structure is of great importance to the mass transport (BRAUCH 1974, HÖLZEL 1975).

Fig. 11: Surface structure of an activated carbon

In Fig. 11 the pore structure of an activated carbon produced from charcoal is shown. One can see that the wood-derived structure is very regular and that the pores are easily accessible. However, it appears that the residual carbon volume is insufficient for the micropores, so that the carbon has only a small capacity.

A completely different appearance is shown by the pressed (extruded) carbon in Fig. 12.

Fig. 12: Surface structure of a pressed carbon

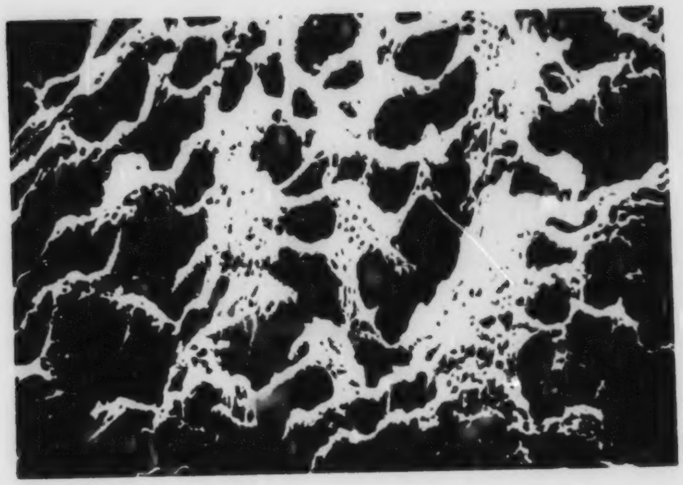
The area illustrated in the figure has a linear dimension of 0.2 mm. It appears that there are no large pores, and if the dark areas represent the position of macropores, they are uniformly distributed and must have a diameter of less than 1 µm.

Again, a totally different picture is obtained of an activated carbon produced from crushed carbonized raw material, as is shown in Figures 13 and 14 (HÖLZEL 1975).

The carbon in Fig. 13 contains a mixture of large and small macropores, while that in Fig. 14 appears to have an almost smooth sintered surface, which is traversed by deep cracks, so that only a limited part of the outer surface is accessible. Thus all the organic material must be transported through the few cracks into the inside.

Fig. 13: Pore structure of a granular activated carbon made of coal

Fig. 14: Pore structure of a higher activated granular carbon made of coal



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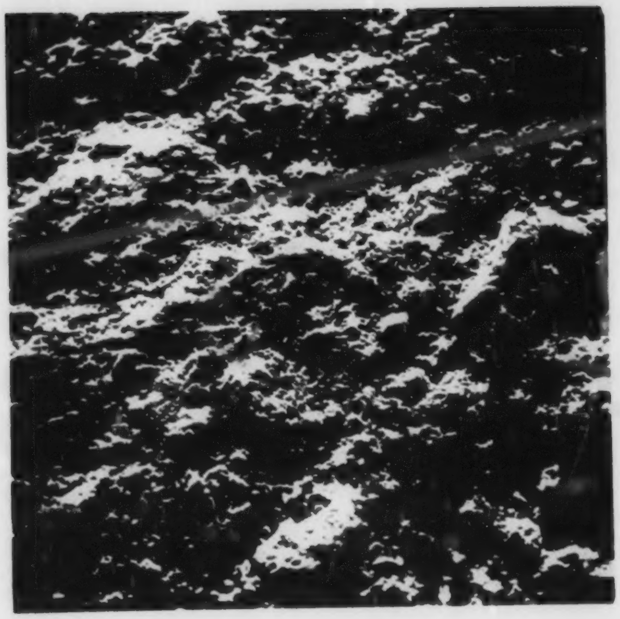

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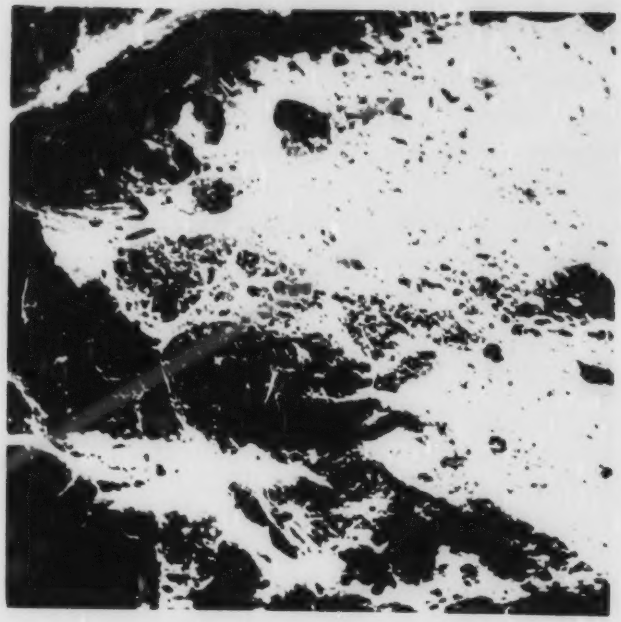


Abb.13

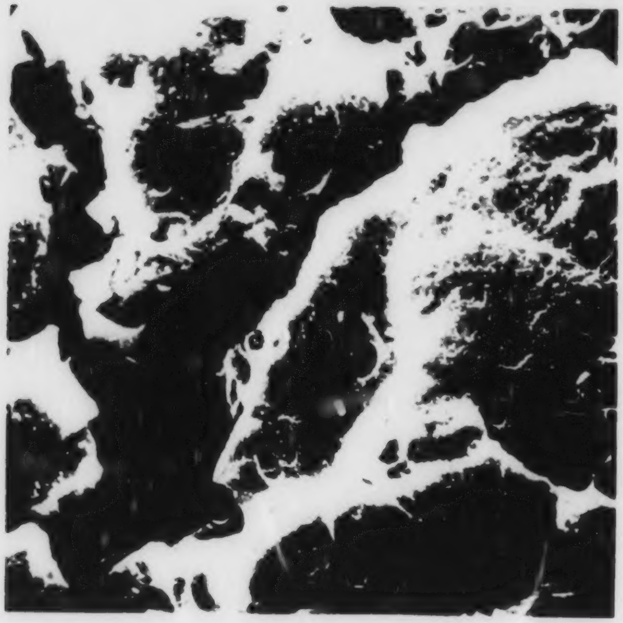


Abb.14

These structural differences make it already clear that major simplifications will be necessary to satisfactorily describe the mass transport during the adsorption process. It is not possible within the scope of these discussions to describe the development of models and their associated mass transport equations. However, it will be tried to clearly set out the information available of the different transport steps. These transport mechanisms are shown in Table 2.

Table 2: Mechanisms of the mass transport during the adsorption of activated carbon

1) Transport in the free liquid
Insignificant in most cases.

2) Film diffusion
The concentration gradient in the liquid film around the granule is the driving force. The transport in the beginning is always rate-determining.

3) Pore diffusion
The concentration gradient in the water-filled pores is the driving force. The concentration in the water enclosed by the pore walls is permanently in equilibrium with the concentration in the carbon phase. This is rate-determining for the mass transport in the easily accessible pores.

4) Surface diffusion
The concentration gradient at the pore surface is the driving force. Rate-determining for the mass transport in the less accessible pores.

5) Adsorption onto the active sites
Very fast in comparison to the diffusional mass transport.

When one considers the adsorption process, it is clear that transport within the bulk liquid to the vicinity of the granule surface must occur before any other step. However, under conditions of practical importance this step is very rapid in a well mixed system. This is followed by the mass transport process through the liquid film surrounding the granule, which initially is rate-determining. The mass transfer coefficient for the film diffusion can therefore be estimated from the limiting slope at time zero (HEIL 1971, SPAHN 1974).

Fig. 15: Film diffusion

Figures 15 and 16 show experimental data and a curve calculated on the assumption that the process is film-diffusion controlled (HEIL 1971). In Fig. 15, even after long times, the process is well described by the film diffusion model. However, in Fig. 16, where a relatively large molecule is being adsorbed, the film-diffusional model is clearly inadequate to describe the mass transfer process.

Fig. 16: Comparison between the measured concentration reduction and that calculated with the aid of the film diffusion model

Today numerous analogous investigations have been carried out under a variety of conditions (see references). In the carbon filters used in waterworks, film diffusion during the first phase of the filter time has an important influence (WEBER 1972). Initially a high flow velocity and a deep layer of carbon would be most effective, that is to say, for a fixed quantity of carbon and a fixed flow rate a narrow high filter would be more effective than a broad shallow filter with a suitable lower flow velocity.

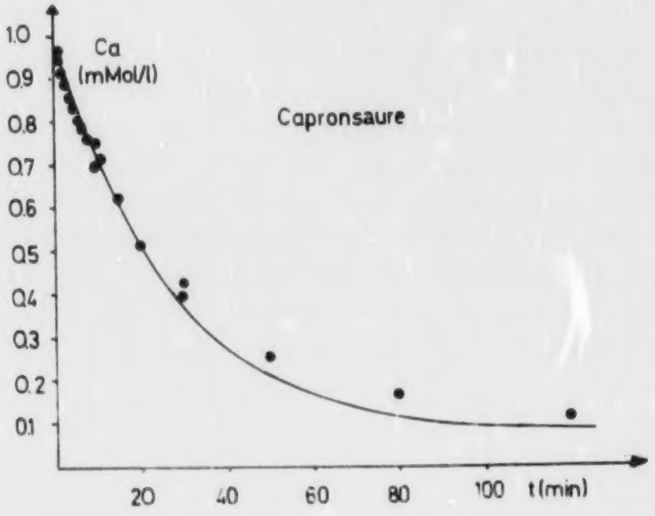


Fig. 15

Capronsäure: caproic acid

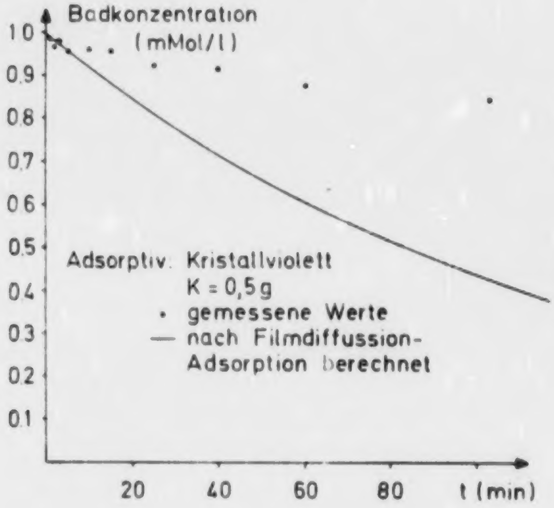


Fig. 16

Badkonzentration: bath concentration

gemessene Werte: measured values

nach Filmdiffusion-Adsorption berechnet: calculated for film diffusion

The influence of film diffusion becomes less important as the carbon is loaded and diffusion within the granule becomes more and more rate-determining. As shown in Table 2, under these conditions it is necessary to distinguish between two mechanisms. In the case of the pore diffusion the driving force is provided by the concentration gradient within the pores. Under these conditions we must remember that the concentration in the pores is permanently in equilibrium with the concentration in the carbon phase. Under comparable conditions a more favourable behaviour should be obtained when the material being adsorbed possesses a favourable isotherm.

Proof of the existence of pore diffusion has been shown in various ways. However, the observation of a moving concentration front, using radioactive-marked organic substances, provides a very clear demonstration (BRAUCH 1974). The results of such an experiment are shown in Fig. 17.

Fig. 17: Experimental proof of irreversible adsorption

Plotted are the test results with radioactive-marked phenylacetic acid on B 10 carbon at different adsorption times. After a loading with marked acid, a further loading with unmarked phenylacetic acid followed, which did not lead to any change of the position of the marked acid.

The sharp loading fronts can vividly be seen in Fig. 17. Other measurements show, however, that there is always an additional transport through surface diffusion too, and that here for example also chemical parameters, especially the affinity between organic substance and activated carbon, can be important. This incident can be recognized very clearly by calculating break-through curves, assuming that there is only pore diffusion (MERK 1975).

Fig. 18: Comparison of measured and calculated break-through curves

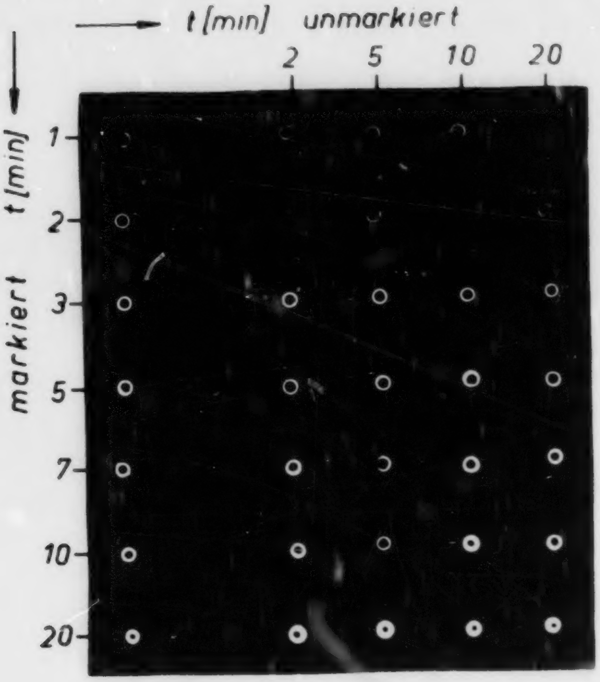

t [min] unmarkiert
2
5
10
20
markiert t [min]
1
2
3
5
7
10
20

Fig. 17: markiert: marked; unmarkiert: not marked

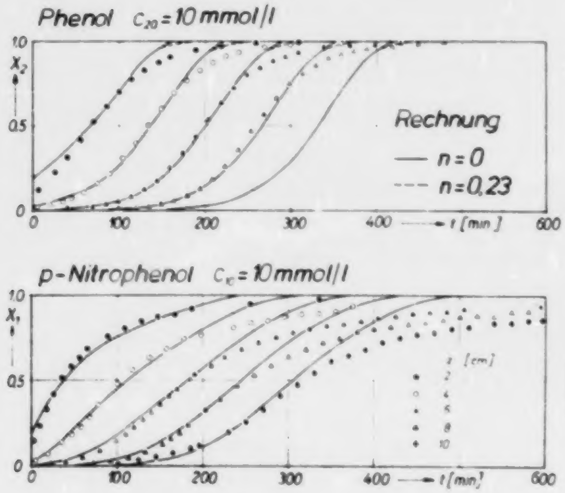


Fig. 18

Rechnung: calculated curve

Calculation and measuring still agree fairly well if one chooses phenol as solute, while the calculation still can be improved by assuming a Freundlich isotherm, as shown in Fig.18. With nitrophenol, however, the deviations become so high that they have to be considered. This can be explained by the fact that the influence of surface diffusion is bigger. It can clearly be imagined that surface diffusion will take place more slowly with a substance of higher affinity to the carbon surface, for this substance is held tight stronger there and is therefore less flexible. A model with which all made observations can be explained can be seen in Fig. 19. Here schematically, with strong magnification, a single transporting pore within an activated carbon granule of a size of about 1 µm in diameter can be seen. The transport to the inside happens within such pores, while a concentration gradient occurs in the pore water. This pore diffusion is coupled with a loading of the adsorption pores within the region of the transporting pores, which are easily accessible. Here primarily a pure pore diffusion appears leading inevitably to building up a sharp front.

Fig. 19: Schematical loading process in an activated carbon pore

Now, not all adsorption pores are that easily accessible. It can rather be expected that certain adsorption fields are situated within the easier accessible regions and hardly opened through transport pores. The organic substances must therefore migrate into these regions along the inner surface of the activated carbon. Through that easier accessible pores become free again and this event brings an additional decrease improving the pore diffusion too. This kind of transport into the hardly accessible pores occurs after the pore diffusion and therefore determines the adsorption kinetics especially at the end of the loading very strongly. Without taking further details into consideration, it will be tried to get some conclusions out of this model. -

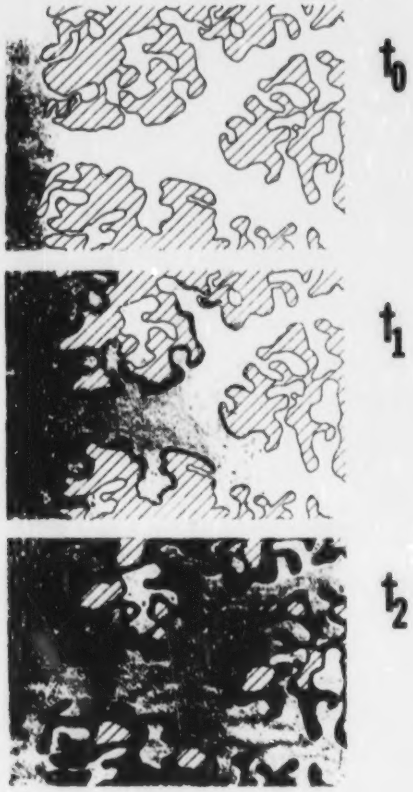


Figure 19

1) Different kinds of carbon have different degrees of easy and hard accessible pores. These differences take effect especially during the second part of the usual filtering time and are especially important for the removal of the better adsorbable substances such as the organo-chloro- and the nitro-compounds. This relationship has to be considered during every way of testing activated carbon.

2) A higher portion of poorly accessible pores will be more important at lower concentrations and with that also at lower equilibrium loadings than at high initial concentrations in the water. That explains the statement that certain kinds of activated carbon can be of advantage at high initial concentrations, whilst others have to be preferred at lower concentrations. Therefore carbon tests should always be done under conditions corresponding to the practical conditions. This is at least necessary as long as there are no common test methods known that would allow a precalculation starting from a general description of the carbon geometry. The measurement of the pore distribution after BET does not bring sufficient information for this.

Behaviour of activated carbon filters

The exact description of the adsorption kinetics on the single granule allows the calculation of the behaviour of filters (BRAUCH et al 1974). Corresponding methods have nearly only been applied successfully for the adsorption of defined single substances. Such an example of calculated break-through curves of phenol and nitrophenol is shown in Fig. 18. Out of this it can be seen that a very exact description of the mass transport in the carbon granule is necessary if one does not want to have strong deviations between calculated and measured break-through curves.

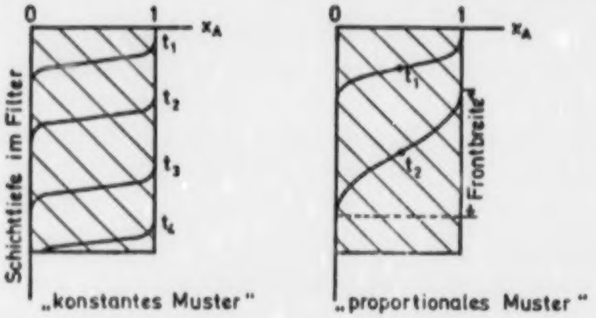
In practice, however, such calculating methods are unimportant because the treated waters always contain mixtures of different substances which are hard to be defined and analysed. Therefore, in the following it is done so that first the basic behaviour of activated carbon will be discussed, and after that the displacement effects at the adsorption of mixed substances shall be examined. Even though no direct consequences for the calculation of the waterworks filters can be taken, such considerations give important indications for the interpretation of practical observations.

One has to take into account that there are two basically different kinds of "break-through" behaviour of activated carbon filters; the constant and the proportional pattern (SPINDLER 1973, Engler-Bunte-Institut Vol. 8, 1975). The corresponding break-through curves are shown in Fig. 20.

Fig. 20: Loading pattern

Most common is the constant pattern which is always achieved if there is a favourable equilibrium. Here the break-through curve has, after a transition region, always the same shape and is estimated through the adsorption equilibrium and through the kinetics.

Entirely different is the filter behaviour at the proportional pattern; this, however, is especially important in the practice of drinking water support. Here a steady extension of the front length occurs with time. The length of the front will be proportional to the way covered, and this means a proportional pattern. Theoretically, such a behaviour is to be expected if a so-called unfavourable equilibrium occurs, meaning the separating factor and the exponent in the Freundlich isotherm are bigger than 1. But that is often observed in practice, as one can see from the isotherms in Fig. 5. In such a case the working


0
1
x_A
t_1
t_2
t_3
t_4
Schichttiefe im Filter
0
1
x_A
t_1
t_2
Frontbreite

„konstantes Muster"

„proportionales Muster"

Fig. 20

Schichttiefe im Filter: bed depth of filter
konstantes Muster: constant pattern
Frontbreite: front width
proportionales Muster: proportional pattern

zone of a filter becomes so long that not the adsorption kinetics but the equilibrium data alone become determining for the effectiveness of the filter. Knowing the isotherm one can precalculate the break-through curve for every filter in a very simple way (DE VAULT 1943, PERRY 1974).

Considering the practical use, it is not quite as simple because for large organic molecules there is always still the influence of the adsorption kinetics. Besides that steep isotherms with exponents over 1 are only achieved if one uses sum parameters, so that the steep isotherm is caused through the different ability of adsorption of different substances.

It is quite helpful anyway if in such cases one calculates as if one had only one substance which behaves according to the isotherm. With that one can make helpful comparisons between different activated carbons, leading to results which can be observed in practice too.

For the practice of waterworks, however, the constant pattern is important too. For example, the adsorption behaviour of especially well-adsorbable organo-chloro compounds can be described in this way. Here one can precalculate fairly exactly by using the measurements in the upper layer of a filter, when a break-through at the end of a filter can be expected. One of the methods used for this is the LUB method, whose principle can be observed in Fig. 21 (COLLINS 1967).

Fig. 21: Break-through behaviour of a filter
Definition by LUB

Here such a constant shape of the front is assumed, which goes through the filter with a constant speed. The measuring of a break-through curve at a given speed allows an exact filter calculation, which will not be discussed in further detail here. There are still a number of similar calculating methods (PERRY 1974).

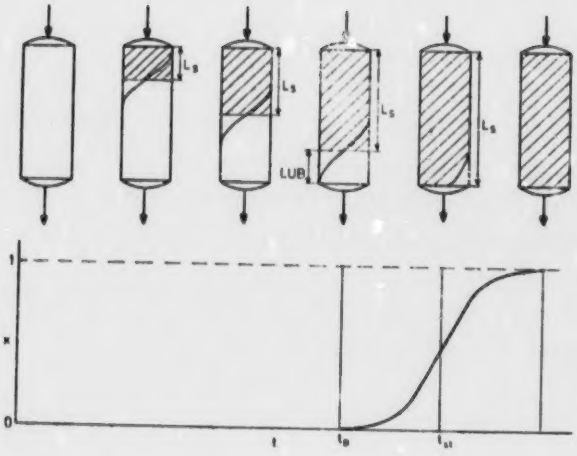

Ls
Ls
Ls
Ls
LUB
1
x
0
t
tB
tst

Abb.21

On the other hand, the front form, meaning the shape of the break-through curve, is seldom as S-shaped as it is shown in Fig. 21. Generally, in practice one can distinguish between two cases. The case with mainly film diffusion and the one when the adsorption kinetics is determined by the diffusion within the grain. Then one achieves different shapes of a break-through curve, as shown in Fig. 22.

Fig. 22: Break-through curves

In the first case we have an early break-through of low concentration, while then, if the grain diffusion is rate-determining, a so-called tail formation occurs. The latter will occur remarkably more often.

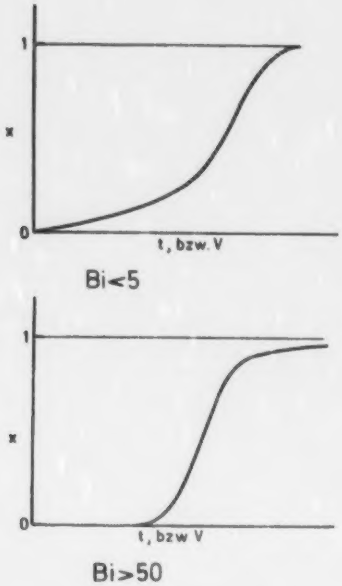
Such influences on the tail shape can also be calculated, as shown in Fig. 23 (MERK 1975).

Fig. 23: Progress of water loading

In the upper part of this figure one can see how an increasing film diffusion coefficient, meaning a decreasing resistance in the film, leads to sharper tails. A similar behaviour can also be observed at higher diffusion coefficients within the granule, because a faster transport of the organic substance will occur.

Apart from this, the steepness of the isotherm or the size of the separating factor influences the shape of the break-through curves, as it can be observed in Fig. 24 (MERK 1975).

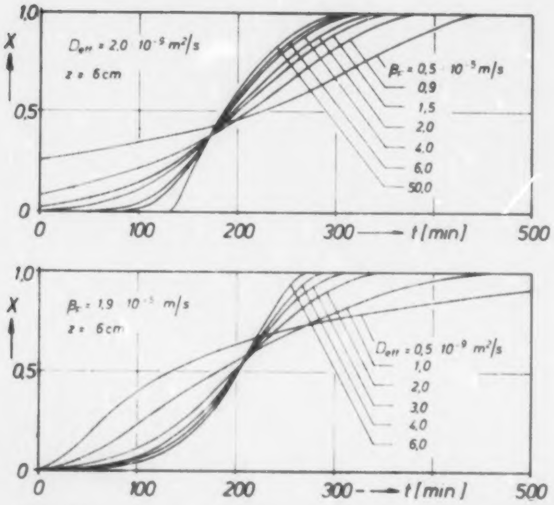
Fig. 24: Progress of water loading at different adsorption exponents



Bi<5

Bi>50

Abb.22



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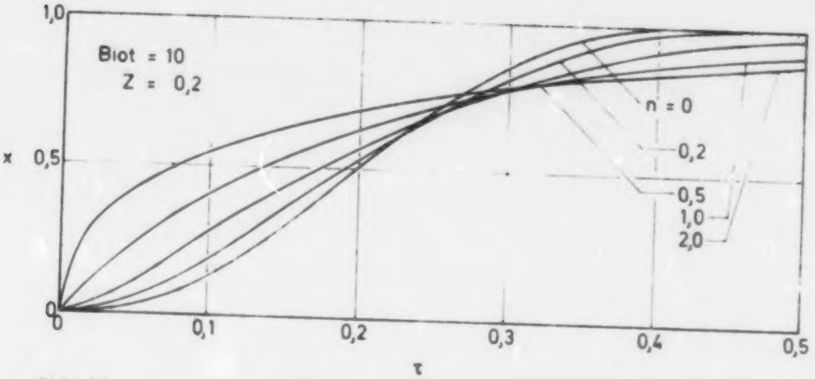


Abb. 24

The more flat the isotherm, i.e. the smaller the adsorption exponent, the steeper is the break-through curve and the more favourable is the behaviour of the filter.

These remarks show how difficult it will be to make relevant predictions for practice even if the loading curves for 5 different substances of wastewater, depending on the bed length, look almost like theoretical curves (KÖLLE et al 1975).

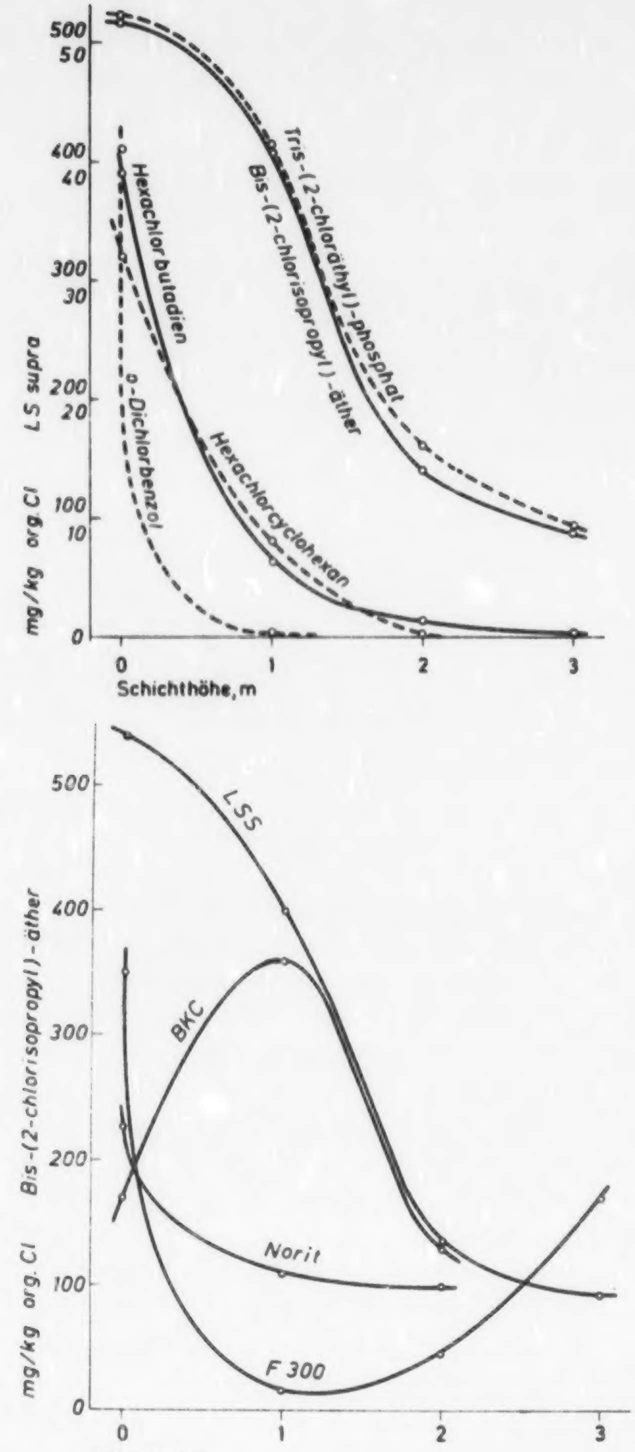
Fig. 25 shows that the most favourable adsorbable dichlorphenol has the smallest break-through pattern, while this is nearly 3 m long for the two polar chlorine compounds. Contrary to all other substances one gets also the typical S-shape, where a tail formation, meaning a strong influence of grain diffusion, appears.

But this picture changes dramatically if one observes the analogous curves for a stronger polar substance such as chlorisopropyl ether at other carbon qualities (KÖLLE et al 1975).

Fig. 25: Adsorption of organo-chloro compounds in an activated carbon filter (KÖLLE)

In Fig. 26 a re-increase of the loadings at the filter end, and in one case even a clear maximum of carbon loading in the middle of the filter, can be observed. Such a behaviour can only be explained if displacement effects occur within the filter because of competitive adsorption.

Fig. 26: Adsorption of organo-chloro compounds onto activated carbon (KÖLLE)



Figs. 25 and 26: Schichthöhe: filter height

The meaning of such effects can be noticed best out of investigations with the already discussed phenol-nitrophenol system, in which the nitrophenol is able to displace the phenol out of the activated carbon. By leading such a mixture through an activated carbon filter one can observe a behaviour of the break-through curves in different bed lengths, as shown in Fig. 27 (MERK 1975).

Fig. 27: Measured break-through profiles at competing adsorption of p-nitrophenol (1) and phenol (2)

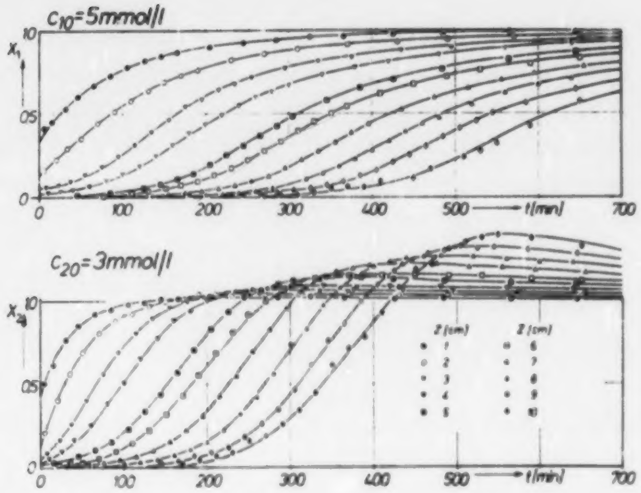
While the break-through curves for nitrophenol have a habitual S-shaped course, at phenol a higher concentration at the filter end occurs than in the entrance after some time, attributed to the displacement effects. Even within the single granule, as FRITZ (1975) could show through his calculations, such displacement effects occur. That can be seen in Fig. 28.

Fig. 28: Concentration profiles in the granule at competing adsorption of p-nitrophenol (1) and phenol (2)

Here the loading scales are drawn in as they move from the right to the left into the center of the granule. The continuous curve stands for nitrophenol, the interrupted one for phenol. The latter substance, as can be noticed, will be displaced from the outside to the inside during the adsorption. As soon as the nitrophenol has also moved inwards, the phenol is displaced again out of the carbon.

This displacement effect can also be proved in the batch test if a phenol-preloaded carbon is put into a nitrophenol solution (FRITZ 1975).

Fig. 29: Investigation of the displacement phenomena on activated carbon in a beaker test



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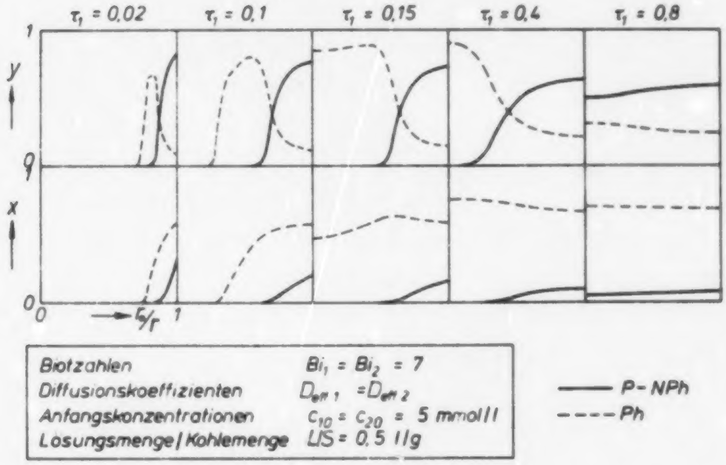


Fig. 28

Biotzahlen: biot numbers

Diffusionskoeffizienten: diffusion coefficients

Anfangskonzentrationen: initial concentrations

Lösungsmenge/Kohlemenge: amount of solution/amount of carbon

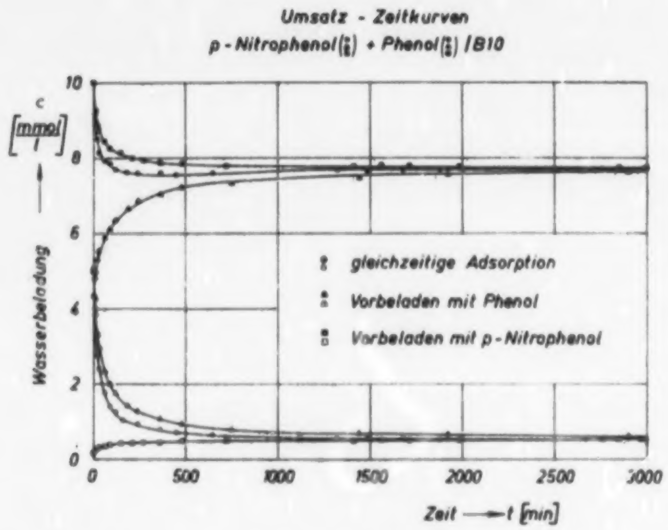


Fig. 29

Umsatz - Zeitkurven: change of concentration with time
gleichzeitige Adsorption: simultaneous adsorption
Vorbeladen mit Phenol: preloading with phenol
Vorbeladen mit p-Nitrophenol: preloading with p-nitrophenol
Wasserbeladung: concentration in water
Zeit: time

Then, as shown in Fig. 29, the concentration of nitrophenol within the solution decreases, while at the same time the phenol concentration increases, because it is displaced out of the carbon into the solution. Such a displacement of already adsorbed phenol occurs within the filter too and causes the concentrations at the filter end to be higher after a certain time than at the entrance.

If the loading of phenol is plotted versus the filter bed length, one will achieve curves as shown in Fig. 30.

Fig. 30: Process of carbon loading with phenol in an activated carbon filter

Here it can be noticed very clearly that for phenol a maximum of loading in the middle of the filter is observed after a certain time, exactly the same behaviour as was observed at one of the test filters in practice for chlorisopropyl ether (see Fig. 26).

These effects show that in practice of drinking water support such displacement effects happen effectively, and wanting to avoid that the concentration of any harmful substance is higher at the filter outlet than at the entrance, those effects have to be taken into consideration.

But this is easier said than done. One of the main problems in registering and taking into account such effects is within the problems corresponding to the analytics, as much as the question of the importance of certain concentrations of harmful substances. Additionally, the concentration and the kind of organic substances within the water can change during a filter run.

Because of this reason one had to rely so far on the use of sum and group parameters in order to predict the working-time of a filter and with that to rely on indirect conclusions for the effectiveness of the filter. Additional single-substance measurements, as they are done at different places

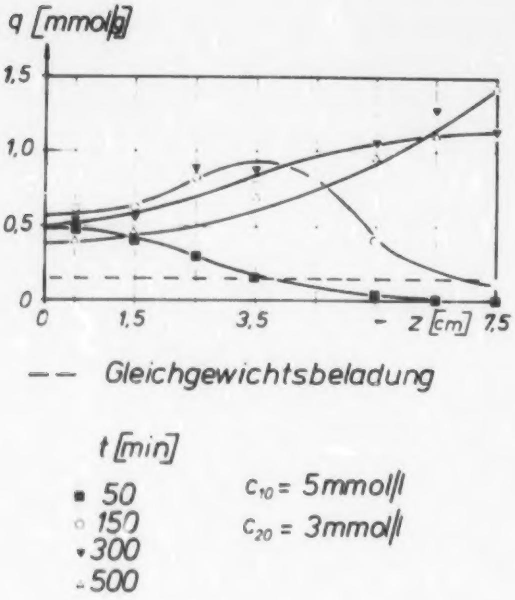


Fig. 30:

Gleichgewichtsbeladung: equilibrium loading now, can help to improve the models used so far and to optimize the use of adsorption plants.

This task requires solid knowledge about the unit operations of adsorption and their use for the interpretation of practical observations. In this way theory and practice complement each other for the benefit of drinking water treatment.

THE USE OF POWDERED ACTIVATED CARBON

by H. Sontheimer

The use of powdered activated carbon in drinking water treatment is far more common than the use of activated carbon filters. It may be estimated that about 90 per cent of the waterworks all over the world which use activated carbon use it in the form of powder (HANSEN 1975). However, in the Federal Republic of Germany the situation is exactly the opposite; a number of factors are responsible for this development.

Nevertheless, before going into further detail, some remarks should be made on the treatment procedure for using powdered carbon and the problems resulting from it. For this purpose, it is helpful to look at the schematic layout of a normal drinking-water treatment plant using surface water.

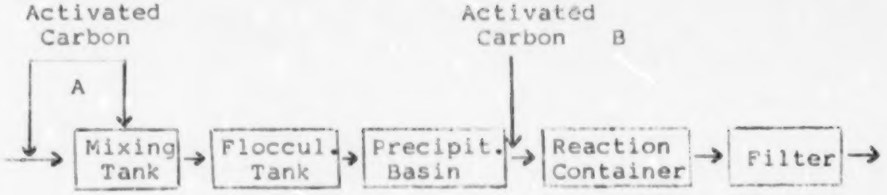
Fig. 1: Possibilities for the use of powdered carbon in the treatment of surface waters

The treatment process illustrated in Fig. 1 includes flocculation and sedimentation, followed by filtration. There are two stages at which the carbon can be added for removing taste and odour substances. These stages are indicated by A and B. Both methods are of some importance for practical use.

The big advantage of adding the carbon at stage A is that, apart from the dosage equipment, no additional equipment is necessary. Furthermore, the length of time required for flocculation is nearly always sufficient for adsorption. Using this method, there are no particular problems in separating the extremely small carbon particles because these are embedded within the flocs.

However, the advantage of this method implies, at the same time, a considerable disadvantage. For one thing, the encasement of the carbon particles will impede the adsorption kinetics, and it will therefore take much longer until the

Fig. 1


Activated Carbon
A
Activated Carbon B
Mixing Tank
Floccul. Tank
Precipit. Basin
Reaction Container
Filter

Single-step dosing of powdered carbon:

Dosage at A : lengthy reaction time; no additional equipment required; interrupted adsorption caused by a coating and by the flocs

Dosage at B : additional reaction vessel required; problems with filtration; better efficiency because of extensive preliminary purification.

Consecutive multistage treatment:

Dosage at A and B: lower consumption of activated carbon; higher investment costs.

final equilibrium is reached. Another point is that by this method a number of substances are adsorbed which would have been removed by flocculation alone. Therefore, more activated carbon is needed. Nevertheless, there have been cases where this disadvantage was compensated by the fact that, due to the presence of activated carbon, flocculation was improved, so that the use of activated carbon leads to a saving of flocculants.

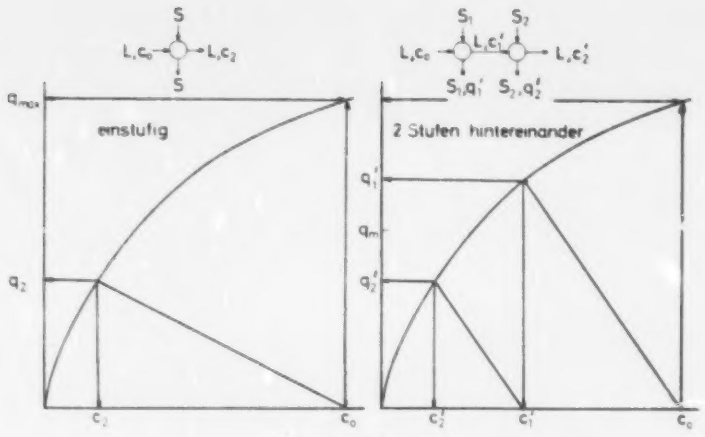
If the activated carbon is added at stage B, it has only to adsorb those substances not removed by flocculation and precipitation. Thus it is possible to choose a specific carbon type with high efficiency. But an additional reaction vessel will be required if the carbon is to be utilized completely. Also, in some cases, the minute carbon particles are not sufficiently retained by the filter. The simplest remedy for this defect is to add a small amount of flocculant before the filter. Today,polyelectrolytes are preferably used for this purpose.

It is also possible, in principle, to divide the activated carbon and to add one half at stage A and the other half at stage B. By this method the amount of activated carbon needed to obtain the same residual concentration is smaller, which can be seen from the diagram shown in Fig. 2.

Fig. 2: Comparison of operational charts for single-step and two-step use of powdered carbon

The diagram on the left illustrates the change in residual concentration and loading when activated carbon is added to the water. The system follows the operating line until it reaches equilibrium (EBI 1974).

It can be seen from the diagram that the load q_2, in equilibrium with the desired low residual concentration c_2, is comparatively small. This is the main drawback of using



$\boxed{S > S_1 + S_2} \boxed{q_2 < q_m}$

$$L(c_0 - c_2) = S \cdot q_2$$

$$S = \frac{L(c_0 - c_2)}{q_2} = \frac{L(c_0 - c_2)}{K_F \cdot c_2^n}$$

$$(c_1/c_2)^n - n \cdot c_0/c_1 = 1 - n$$

$$S_1 + S_2 = L(c_0 c_1^{-n} - c_1^{1-n} + c_1 c_2^{-n} - c_2^{1-n}) \cdot 1/K_F$$

Fig. 2:

einstufig: **single-step**

2 Stufen hintereinander: **two-step, consecutive**

S = amount of carbon (kg)
q = carbon load (g/kg)
L = volume of water (m^3)
c = concentration of substances to be removed (g/m^3)
c_o = initial concentration
q_{max} = load at equilibrium - the equilibrium concentration being equal to the initial concentration

powdered carbon because in most cases the highest maximum load possible - which may be attained in a sufficiently large carbon filter - is almost three times as high. Thus, quite often the consumption of powdered carbon is twice as high than if granular activated carbon is used in filters.

Some improvement can be made by a two-step dosing, as shown in the diagram of Fig. 2. Here the amount of carbon is divided and added in two consecutive doses. By this type of process one half of the carbon is more heavily loaded and, corresponding to the relation of q_2 to q_m, carbon consumption can be reduced; but, at the same time, more equipment is necessary. The amount of carbon required for each stage can be calculated from the formulas listed in Fig. 2. However, when put into practice, this method does not seem worth-while because in most cases the advantage is too small. Nevertheless, in some special cases it may be interesting to use a different type of carbon at either stage, thus having the advantage of a carbon mixture (BALDAUF 1974).

For the sake of completeness, mention should be made of another technical possibility for the use of powdered carbon, i.e. the depositing of the carbon, usually together with kieselguhr,/(diatomaceous earth) in a filter cake through which the water to be treated is filtered. In addition to the deposited material there is nearly always a continual dosing of carbon (VOSTRCIL 1971, KURAPKAT 1963). This treatment process has some similarity to the effectiveness of an activated carbon filter. In recent years this process has frequently been used for drinking water treatment, especially in those cases where the water contained coloured substances. Particularly good results were obtained with raw waters from lakes, which only required an occasional treatment with activated carbon (SYMONS 1975).

The pros and cons of using powdered activated carbon, based on experience and information available so far, are listed in Table 1.

Table 1: Advantages and disadvantages of using powdered activated carbon

Advantages:

1) Easy adaptation to changes in water quality
2) Low investment costs

Disadvantages:

1) High operating costs
2) No regeneration of the activated carbon
3) Poor efficiency for DOC removal
4) Additional sludge problems
5) Problems of complete removal of minute carbon particles

It would therefore seem that the use of powdered activated carbon is most advantageous in those cases where an adsorbent is required only occasionally or where the demand of activated carbon varies considerably. Activated carbon filters must be designed for the poorest quality of raw water, which means that investment costs are high. Treatment with powdered carbon, on the other hand, merely requires stocking a certain amount of carbon. It is possible to start or stop the dosing at very short notice, and also to lower or to increase it. Carbon filters, on the other hand, will rise problems of bacterial growth etc. when the filters are left to stand without water flow.

For this reason, powdered carbon is recommended in those cases where an occasional use of adsorbents is required. The disadvantages listed in Table 1 will be of less importance or, rather, remedial measures can be taken.

However, the above does not apply when activated carbon is required constantly as, for instance, at many places along the Lower Rhine, due to the chemical pollution of the water. For this reason, most waterworks in Western Germany are now using activated carbon filters. However, investigations are being made in some places on whether suspended powdered carbon might be used in a cycle with a cascade system. However, no detailed practical results are available as yet.

ACTIVATED CARBON FILTERS IN WATER TREATMENT PLANTS
PROCESSING TECHNIQUES - ENGINEERING - OPERATION

by W. Poggenburg, Düsseldorf

The general processing techniques developed for the treatment of Rhine-bank-filtrate, the construction and the knowledge and experience gained from running activated carbon filter plants are well illustrated by the Düsseldorf drinking water supply.

Since 1961 the city of Düsseldorf has processed natural ground water, which is influenced by the condition of the Rhine water, using ozone and activated carbon to produce drinking water. The producing plants Flehe, Staad and the Wuppertal and Lower Rhine-Bergische waterworks are all situated on the Rhine, with well centers 50 m to 250 m from the bank.

Fig. 1: Bank filtration

The bank filtration

The ground water is extracted in vertical and horizontal wells from large 10 m to 30 m water-bearing diluvial gravel and sand sediments. The raw water consists mainly of bank filtrate, together with a small amount of ground water inflow from the Bergische Land.

Normally, the ratio of bank filtrate to ground water is about 3 to 2, but it varies with the water level of the river and changes in the water-table. The natural treatment effect of ground passage on the bank filtrate between the Rhine and the well should not be underestimated. During ground passage there occur numerous mechanical, biological and chemical processes. Turbidity and, included with it, associated organic and inorganic susbstances such as pesticides, heavy metals and bacteria are retained in the gravel and the sandstone sediment. The combined bank filtrate and ground water in the wells is clear and almost

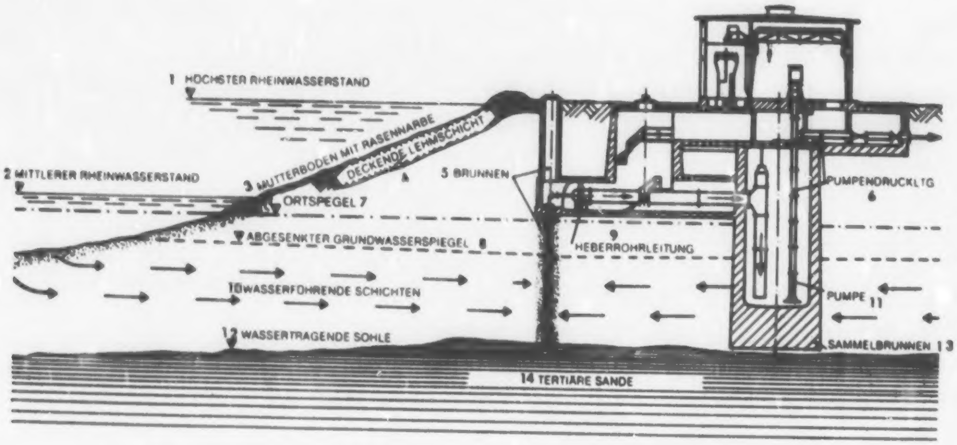

1 HÖCHSTER RHEINWASSERSTAND
2 MITTLERER RHEINWASSERSTAND
3 MUTTERBODEN MIT RASENNARBE
DECKENDE LEHMSCHICHT
4
5 BRUNNEN
PUMPENDRUCKLTG
6
ORTSPEGEL 7
ABGESENKTER GRUNDWASSERSPIEGEL 8
9
HEBERROHRLEITUNG
10 WASSERFÜHRENDE SCHICHTEN
PUMPE 11
12 WASSERTRAGENDE SOHLE
SAMMELBRUNNEN 13
14 TERTIARE SANDE

Fig. 1

1 Höchster Rheinwasserstand: maximum water level of the river Rhine
2 Mittlerer " : medium
3 Mutterboden mit Rasennarbe: top soil with grass cover
4 Deckende Lehmschicht: covering clay layer
5 Brunnen: well
6 Pumpendruckleitung: pressure pipe
7 Ortspegel: level control
8 Abgesenkter Grundwasserspiegel: reduced ground-water level
9 Heberohrleitung: siphoning installation
10 Wasserführende Schichten: ground-water transporting layers
11 Pumpe: pump
12 Wassertragende Sohle: water-bearing layer
13 Sammelbrummen: collecting well
14 Tertiäre Sande: tertiary soil

always bacteriologically acceptable. It contains, however, soluble iron, manganese and other inorganic and organic compounds which are not removed during ground passage. These substances, either because of their bad taste and odour characteristics, or due to their possible harmfulness to human life, have to be removed as far as possible in the water treatment plant.

The treatment process

The treatment processes used by the Rhine waterworks have been developed as the result of a close interchange of information between the waterworks in cooperation with the Engler-Bunte-Institute at Karlsruhe, and have been adapted to meet the conditions existing at present.

Fig. 2: The treatment process

In Düsseldorf the treatment of the raw water obtained in the wells takes place in four processing steps.

Step 1:
Oxydation of the impurities by ozonization.

Step 2, upper activated carbon layer:
Reduction of permanganate to manganese dioxyde, filtration, operation of biological processes.

Step 3, lower activated carbon layer:
Adsorption and operation of biological processes.

Step 4:
Removal of aggressive carbon dioxyde in the main distribution pipes by addition of sodium hydroxide.

Fig. 3: The first processing step

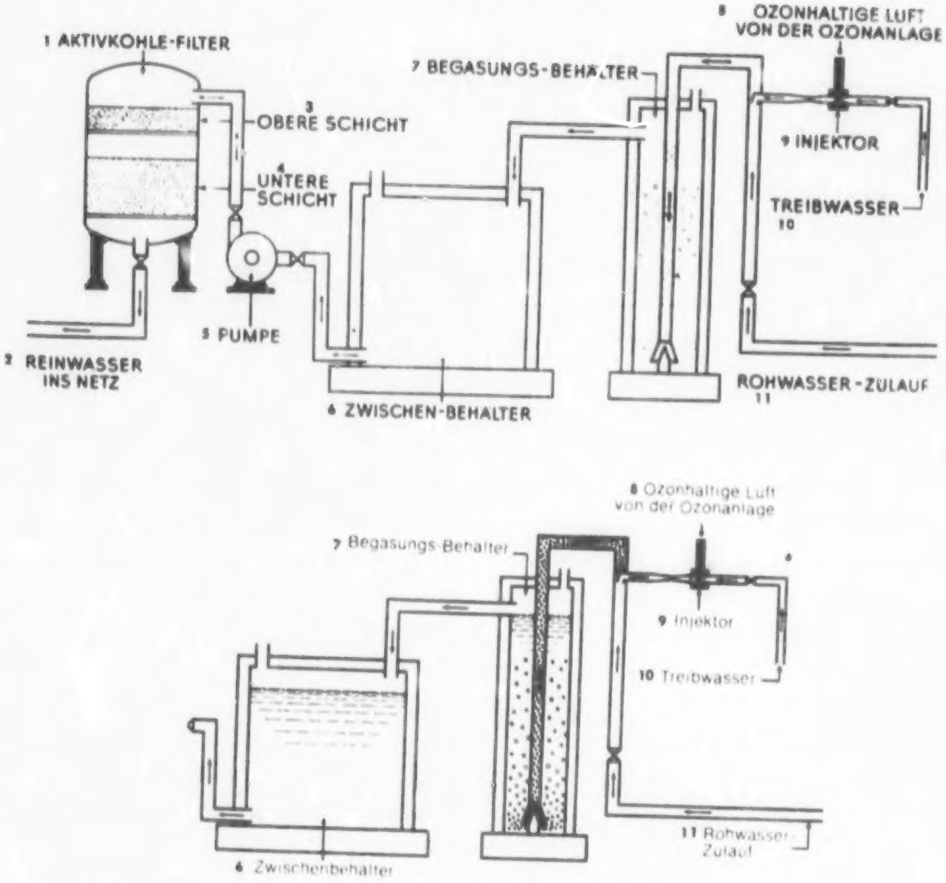

1 AKTIVKOHLE-FILTER
3 OBERE SCHICHT
4 UNTERE SCHICHT
5 PUMPE
2 REINWASSER INS NETZ
6 ZWISCHEN-BEHALTER
7 BEGASUNGS-BEHÄLTER
8 OZONHALTIGE LUFT VON DER OZONANLAGE
9 INJEKTOR
TREIBWASSER 10
ROHWASSER-ZULAUF 11
8 Ozonhaltige Luft von der Ozonanlage
7 Begasungs-Behalter
9 Injektor
10 Treibwasser
11 Rohwasser-Zulauf
6 Zwischenbehalter

Fig. 2 and 3

1 Aktivkohle-Filter: activated carbon filter
2 Reinwasser ins Netz: treated water
3 Obere Schicht: upper layer
4 Untere Schicht: bottom layer
5 Pumpe: pump
6 Zwischen-Behälter: intermediate container
7 Begasungs-Behälter: gassing tank
8 Ozonhaltige Luft von der Ozonanlage: ozone-containing gas from ozone generator
9 Injektor: injector
10 Treibwasser: carrier water
11 Rohwasser-Zulauf: raw water inlet

Only a short description of the first processing step is given, as it gives a better overall view. However, some particular details are of general interest.

Water-jet injectors introduce the ozone-containing air into the pipes leading to the gas adsorption tank. Using this technique, good mixing and an intimate contact of the gas and the raw water is obtained.

The ozone, which is produced from air in tube ozonizers having a potential of 16,000 volts, is used to oxidize organic and inorganic compounds in the water, part of which may be removed as a filterable suspension. The gas mixture contains 35 g/m^3 ozone, at a pressure of 1 bar, and has a contact time of 5 min. To achieve an adequate degree of oxidation, as the amount of harmful material increases, up to 3 g ozone/m^3 water have to be added today, whereas previously 1 g/m^3 was sufficient.

This method used at Düsseldorf is not practised everywhere, however. Ozone can also be obtained from pure oxygen. It is also possible to dissolve the gas countercurrently in washing- or mixing tanks using the pressure in the water supply pipe.

If the ozone is added in a closed process immediately before the activ. carbon plant, which is under supply water pressure, the production of oxygen is unavoidable. The undissolved gases are dried and recycled.

After ozone, potassium permanganate or chlorine may be applied.

Fig. 3 a: Tube ozone generator

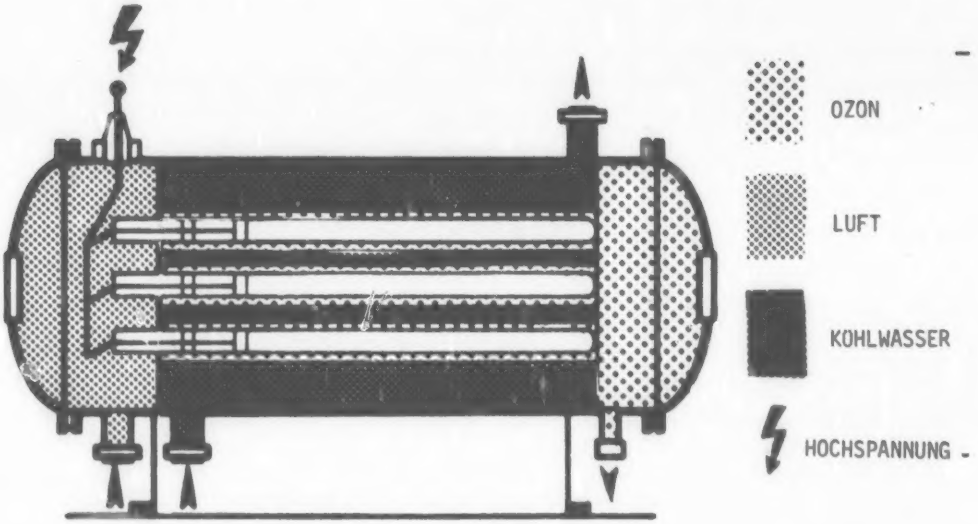

OZON
LUFT
KÜHLWASSER
HOCHSPANNUNG

Fig. 3a

Ozon: ozone

Luft: air

Kühlwasser: cooling water

Hochspannung: high voltage

At Düsseldorf, the water flows from the gas adsorption tank to two large intermediate storage containers where after-reaction and degasification occur. The retention time of the water in the container is at least half-an-hour. The residual ozone-containing air is discharged to the atmosphere through special treatment plants. Originally, the residual ozone was removed by contacting it with loaded activated carbon. As a result of operating disturbances on higher ozone dosages, larger amounts of exhaust air are discharged, which may result in ozone break-through. For the past few months special catalysts have been tested at the treatment plant at Staad to remove the ozone from the exhaust air. The results obtained so far show that the catalysts are effective even under the most unfavourable conditions. However, still unknown is the effective life of the catalyst.

The residual ozone content of the exhaust air is at a maximum 3 per cent of the generated ozone, giving an efficiency of ozone consumption of more than 97 per cent.

The activated carbon filter plant - processing steps 2 and 3

Operation and construction of the activated carbon filters

From the surge tanks the water is pumped, using centrifugal pumps, at full supply pressure - 6 to 7 bar - into the two-stage activated carbon filters. The filters are constructed of steel and are 8 m high, with a diameter of 5 m. The water enters at the top of the filter through distributors and passes through two layers of carbon. Each layer rests on a support plate which contains 632 plastic jets, about 31 per m^2.

A layer of gravel of various size fraction lies between the support plate and the activated carbon. The medium velocity in the filter at present is 22 m/h. However, to obtain a better filtrate, as a result of a longer contact time with the activated carbon, the plant has been enlarged and the velocity reduced to 12 m/h.

Operations of the plant at 20 m/h also produced problems in running the filters in that an even layer of carbon in the upper sections was not always obtained. Scouring of up to 70 cm was noticed. This was eliminated by modifying the distribution system and reducing the entry velocity of the water.

Fig. 4: Protection of the upper jet support plates

The support plates are designed for a working pressure differential of 1 bar, while new plants are designed for a pressure differential of 2 bar. To protect the upper plate, which is most likely to be overloaded, bypass pipes with rupture disks are installed. The failure of a rupture disk is signalled to the filter control panel and the corresponding filter is then immediately removed from service.

To minimize corrosion in the inner parts of the steel filter, it is coated with a physiologically inert two-component material. The coating thickness varies between 0.4 mm and 1.0 mm. To ensure good durability, the steel surface must be sand-blasted and treated according to DIN 28051 before the application of the coating. The first activated carbon filters were put into service in 1961. Up to the present time none of the filter coatings have had to be renewed, except in parts which were damaged by mechanical wear. This was the case, after ten years of operation, with the carbon filling- and flushing connecting pipe.

Activated carbon filters are not only produced as steel pressure filters but also from reinforced concrete, in rectangular form, and also as open filters for pressureless running. The type of filter and materials of construction may be determined on economic and technical grounds. At high operating pressure, steel filters are used exclusively. With open filters and at low operating pressure, construction of steel or reinforced concrete is possible. Reinforced concrete filters do not require any special coating but must be made waterproof following DIN 1045 and, to insure

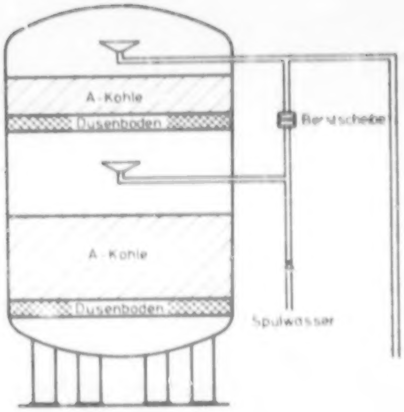

A-Kohle
Düsenboden
Berstscheibe
A-Kohle
Düsenboden
Spülwasser

Fig. 4

A-Kohle: activated carbon
Düsenboden: jet support plate
Berstscheibe: safety disk
Spülwasser: backwash water

the protection of the reinforcing steel, the concrete should cover it to at least 5 cm, according to DVGW paper W 111. Large stainless steel filters are unlikely to be installed because of the high cost of construction. However, an internal coating is also recommended in stainless steel filters to eliminate the possibility of corrosion, even though it may not be strictly necessary.

The second processing step

In the second processing step the manganese,which has been converted to pyrolusite, and other suspended material produced in the oxidation process are removed in the upper layer of the activated carbon by filtration.

Fig. 5: Second and third processing step

Until recently, the filter material was an activated charcoal with a granule size of between 0.5 and 2.5 mm. The height of the layer was 1 m. It was found over the years that the charcoal was inadequate as a filter material as well as for the separation of ammonia. A considerable fraction of the suspended material passed through the upper layer to the lower layer, which is used for the adsorption of organic material.

Extensive experiments have been undertaken to improve the effectiveness of this processing step. Experiments in which a prior flocculation was carried out produced no worth-while improvement. Numerous filter materials, both alone and in various combinations, were tested in small and large filters to produce a both technical and economical solution. The problem appeared to be to find a filter material which in its granulation and pore-size distribution would suit the conditions existing in the filter.

It was found that either,when good-quality filtrate was obtained, the operating times were very short or the pressure differential was unacceptably high. The quality of the filter material was judged on turbidity measurements, running time, the pressure drop dependence on flow velocity as well as the determination of the behaviour of the start-up, operation and flushing. The pressure drop was measured at various depths in the layer of the activated carbon. The presupposed limiting conditions for the filtration were:

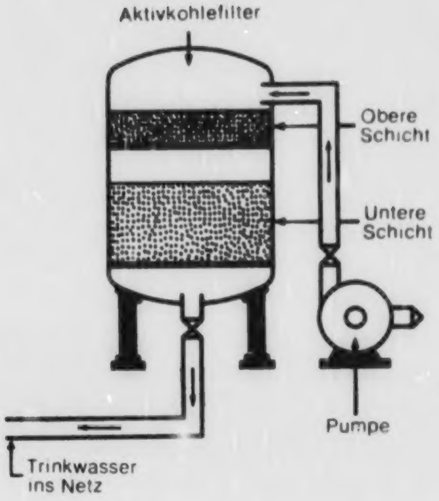

Aktivkohlefilter
Obere Schicht
Untere Schicht
Pumpe
Trinkwasser ins Netz

Fig. 5

Aktivkohlefilter: activated carbon filter

Trinkwasser ins Netz: drinking water to the supply system

Obere Schicht: top layer

Untere Schicht: bottom layer

Pumpe: pump

Removal of

manganese to 0.5 g/m^3 ozonized water
iron to 0.1 g/m^3 ozonized water
filter velocity 20 m/h
maximum pressure drop 600 mbar
layer height 1.8 m

The values aimed at were:
manganese not detectable
iron not detectable
running time 48 hours
surface loading 1000 m^3/m^2

Although not all the problems, especially the theoretically interesting ones, have been solved, it can be said already now that the tests have been successful.

The desired values were best obtained with an intermediate product of activated carbon production, a so-called pre-activate.

Characteristic properties of this material:
granule size: 0.9 - 2.5 mm
mean granule diameter: 1.7 mm
bulk weight: 580 kg/m^3

The use of the pre-activate provides a number of advantages at a filter layer height of 1.5 m. They are:

1. Considerable improvement of the filtrate quality and the start-up process.

   There are now no noticeable amounts of filterable material on the lower adsorption layer at reasonable filter running times.

2. The degradation of ammonia which may be present by biological processes (nitrification) is moved from the lower to the upper filtration layer of the filter.

3. Due to the good filtration in the upper layer the adsorption process is necessarily improved in the lower layer.

Because of the pressure drop measurements a layer thickness of 0.5 m would be sufficient for filtration. Most of the filterable substances are retained in the upper 0.5 meters of the carbon layer, Figure 6.

However, the turbidity measurements show that a layer thickness of at least 1.5 m is necessary for the filtration of the finest particles, and to obtain optimum conditions, Figure 7.

The third processing step

In this process step organic compounds are removed in the lower activated carbon layer by adsorption. The activated carbon quality,originally mainly chosen according to its phenol loading to improve taste and odour in the water, has been shown not to meet modern requirements in almost any way.

The further increase in organic load of the mixed ground water, which depends on the quality of the Rhine water, especially of organo-chloro-compounds, was at first balanced by increasing the ozone dosage from initially 1 g to 3 g/m^3, and the activated carbon from 3 g to 10 g/m^3 water. In long-term tests, in co-operation with the Engler-Bunte-Institute and other waterworks, the behaviour of different carbon qualities under different conditions was investigated, especially regarding adsorption capacity and adsorption velocity. The information obtained and more sensitive analytical methods made it possible to get the activated carbon manufacturers to supply carbons of a better and more uniform quality, with higher activity, although they are not quite satisfactory yet.

By this, a further optimization of the third processing step has been achieved. The activated carbons "LS Supra" and "F 300" are mainly used, chiefly as a mixture, with a granule size between 0.5 mm and 2.5 mm, at the Düsseldorf plants. The mean diameter of the carbon granules is 1.4 to 1.6 mm. The carbons are about 40 % heavier than those previously used. No disadvantages were noticed in the operation of the filters, due to the higher particle density.

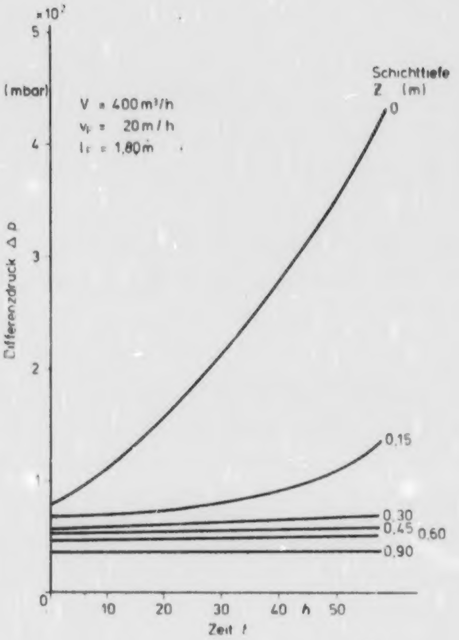


Figure 6. Pressure Differential in the Upper Filter Layer

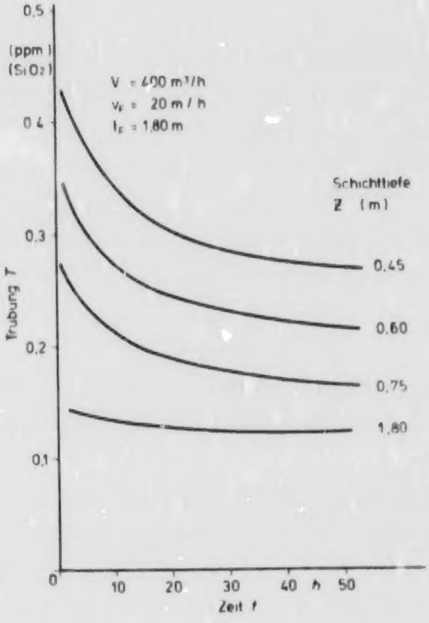


Figure 7. Turbidity in the Upper Filter Layer

Figs. 6 and 7

Schichttiefe: filter bed depth
Differenzdruck: differential pressure
Trübung: turbidity
Zeit: time

Apart from the two carbon types mentioned above, there are other good materials on the market.

Using the better-quality activated carbons, it was possible to achieve a greatly increased removal of organic compounds in the adsorption layer by reducing the operating velocity by about 50 % and by increasing the layer height from 2 m to 2.5 m.

In order to make a valid statement on the influence of the mechanical properties of activated carbon, further investigations have to be made.

A process control procedure, introduced at Düsseldorf, has proved to be very satisfactory. The total dissolved organic content of the water is defined by measuring the UV extinction. For a reliable evaluation, an investigation period of about 8 days is required. However, it is necessary to find a method which makes it possible to detect very rapidly the degree of exhaustion of activated carbon and also the harmful substances in drinking water. This problem has been worked at for a long time. It is hoped that it will be solved shortly in a manner acceptable to the waterworks. This would certainly be an enormous advance.

The effectiveness of bank filtration and of the individual processing steps in water treatment are illustrated in Figs. 8 and 9. In evaluating the effectiveness, it is to be remembered that in the treatment processing steps mainly the organic compounds which are present in small amounts in the water, which are non-biodegradable but which are harmful or even dangerous, are oxidized, altered, filtered out and adsorbed.

Fig. 8: Relative treatment effectivity referred to DOC, COD and UV in 1974

Fig. 9: Mean values of important substances in Düsseldorf drinking water

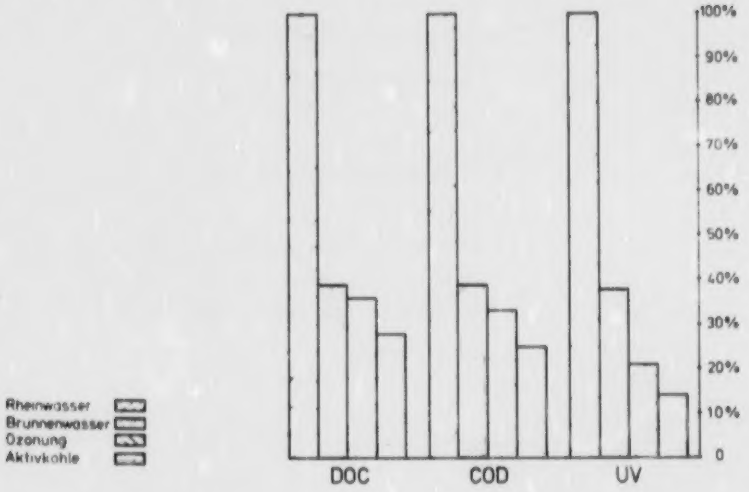


Fig. 8

Rheinwasser: water from the river Rhine

Brunnenwasser: water from the well after bank filtration

Ozonung: ozonization

Aktivkohle: activated carbon

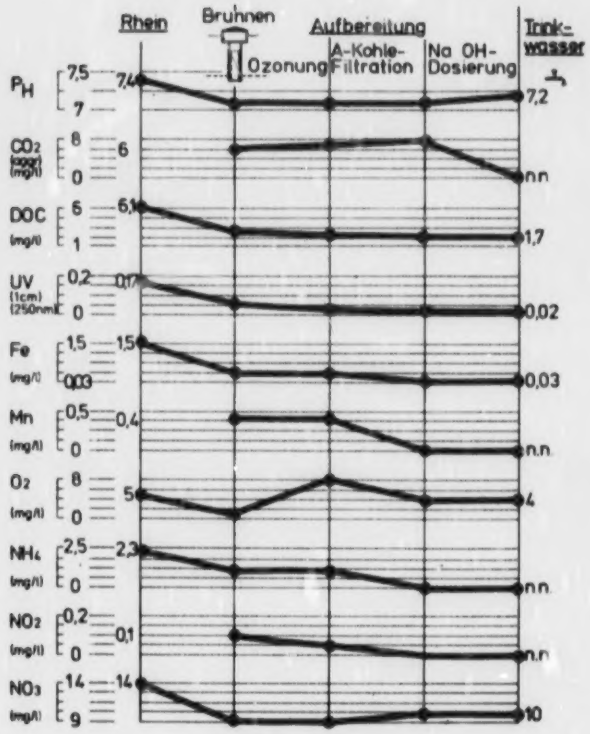


Fig. 9

Rhein: river Rhine
Brunnen: well
Ozonung: ozonization
Aufbereitung: treatment
A-Kohle-Filtration: activated carbon filtration
Na OH-Dosierung: Na OH-dosage rate
Trinkwasser: drinking water

Backwashing of activated carbon layers

After a certain amount of throughput the filters have to be backwashed. This is the case for the upper filter layer after a water throughput of about 20,000 m^3, which means a running time of 50 hours at an operating velocity of 20 m/h.

The running time of the adsorption layer is considerably longer because filterable substances, as already mentioned, do not reach this layer in any appreciable quantity.

By special measures it was possible to reduce the amount of backwash water and the backwashing velocity, although an activated carbon with a higher density was used. The freeboard height, which is the distance of the upper layer of carbon and the backwash discharge pipe, was reduced amongst other things. For backwashing air was used, and then water. The initial resistance of the unsoiled carbon are about 80 mbar in the upper filtration layer and about 120 mbar in the lower adsorption layer.

The measures applied made it possible to reduce the backwash velocity from 30 m/h to about 15 m/h, and the backwash time, using water, from 20 min to about 5 min. Limiting values for the backwashing process are a filter resistance of 600 mbar in the upper layer and 300 mbar in the lower layer at a filter velocity of 20 m/h. The volume of backwashing water is today about 50 m^3 as against 150 m^3 with the previous backwash technique.

The treatment of the backwash water is carried out in special plants. The water is passed from the filters to sedimentation tanks, made of reinforced concrete, the lower parts of which are funnel-shaped. The filtered substances settle rapidly. After a sedimentation time of about 20 min the clear water is drawn off and discharged into a sewer. The settled sludge is pumped to drying beds once a week, and then later incinerated.

Fig.10: Schematic layout of a filter in operation and during backwashing

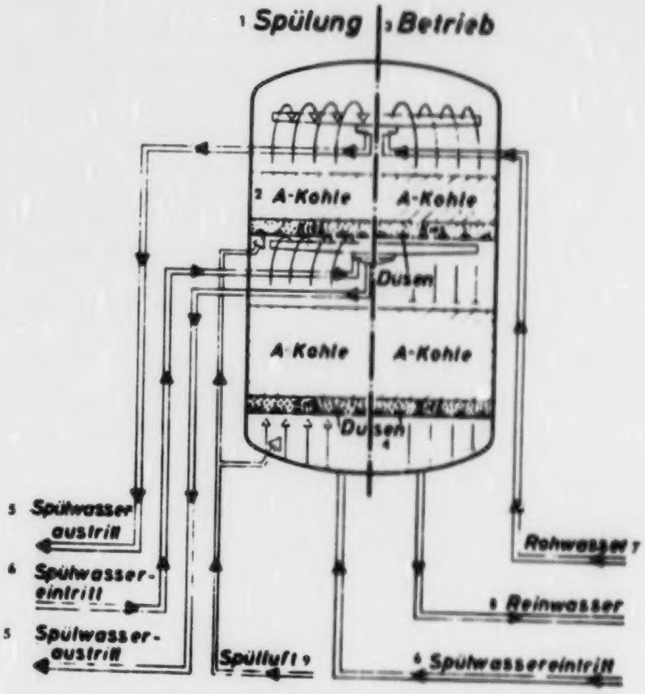

1 Spülung
3 Betrieb
2 A-Kohle
A-Kohle
Düsen
A-Kohle
A-Kohle
Düsen
4
5 Spülwasser austritt
6 Spülwasser-eintritt
5 Spülwasser-austritt
Spülluft 9
Rohwasser 7
8 Reinwasser
6 Spülwassereintritt

Fig. 10

[1] Spülung: backwashing
[2] A-Kohle: activated carbon
[3] Betrieb: filtration operation
[4] Düsen: jets
[5] Spülwasseraustritt: outlet for backwashing
[6] Spülwassereintritt: inlet for backwashing
[7] Rohwasser: raw water
[8] Reinwasser: treated water
[9] Spülluft :air for backwashing

Reactivation of the activated carbon

Whilst the upper activated carbon layer does not need changing, or maybe only very seldom, the lower adsorption layer is exchanged regularly twice a year - previously it was once a year. According to the present evaluation methods - determination of the total organic components by UV extinction - the adsorption capacity is only 20 % after a throughput of between 400,000 m^3 and 600,000 m^3 water per filter and an activated carbon amount of 40 m^3. The adsorption capacity of new or freshly reactivated carbon lies generally between 70 % and 80 %. Taking as a basis this degree of loading and a mean operating velocity of 12 m/h, the activated carbon has to be reactivated or replaced by fresh carbon in each filter four or five times a year.

Due to the problems associated with the reactivation of spent activated carbon at outside firms, it seems advisable that the waterworks had its own plant. Apart from the economy, this contributes substantially towards securing a constant water quality. It is thus possible to adjust the carbon quality to any special requirements at any time, and to have newly reactivated carbon available at short notice in the event of a sudden concentration of harmful substances in the raw water. A reactivation plant with a fluidized bed furnace with a daily capacity of 6 t will therefore be put into operation at the Düsseldorf waterworks. The plant can be extended to a daily capacity of 18 t.

Of course, losses of carbon are incurred in the running of activated carbon plants and the thermal reactivation of activated carbon. The carbon loss in backwashing, operation, transport and reactivation is at present reported to be between 14 % and 15 %. The highest losses are incurred in transport. They are in the range of 10 %. These losses can surely be substantially decreased by on-site reactivation.

Input, extraction and transport of activated carbon

Since 1969, the transport of all activated carbons has been made exclusively in silo transporters.

The carbon is washed into the carbon filter from the silo transporter with the aid of an injector and pressurized water through a transportable steel pipeline or flexible pipes. The tank of the silo transporter is first lifted and inclined by about 60°. If the carbon in the transporter is dry, water is added with a hose pipe until the carbon has the consistency of dough. This has the advantage, amongst others, that the carbon is wetted with water already at this stage and that the degassing period of 24 hours, which may be necessary in some instances, can be considerably reduced.

The filling process can be observed and controlled through a sight glass. In order to prevent the carbon from piling up in the filter, it is necessary to flush with water or air several times during filling. The time required to transport 40 m^3 activated carbon over a distance of 50 m and a filling height of 8 m is about 4 hours, at a bulk weight of about 420 kg/m^3.

The preparation periods for transport, pipelines etc. are contained herein. The ratio of pressurized water to activated carbon is 3 to 1.

When the carbon is flushed from the filters, the filters are kept filled with water and are put under pressure. The silo-transporter is connected by a pipeline system with the appropriate filter.

In order to keep the carbon from settling during the flushing-out process, about 300 m^3/h to 500 m^3/h water is added continuously. Thus it is possible to rinse out even the last remains of carbon.

There are no significant amounts of gravel washed out during this process from the supporting layers into the flushed-out carbon. If a certain amount of gravel is contained in the activated carbon, reactivation is disturbed.

The time necessary for flushing out 40 m^3 activated carbon, including preparation time, is three hours. The actual flushing-out period is about 40 minutes. The filling and flushing-out of the carbon can easily be done by two persons. After the flushing-out process an after-dehydration of 2 to 3 hours of the activated carbon is required to avoid overloading the silo transporter. The silo has to be inclined for this purpose.

Since the installation of the reactivation plant at the Holthausen waterworks, the filling and flushing-out of the activated carbon between filter and storage tank has been made through a fixed pipeline system made of synthetic material. The transport of the activated carbon between the works at Flehe or Staad and the reactivation plant is carried out, as usual, with silo transporters.

In order to save costs, investigations are made at present to reduce the demand of water required for filling and flushing-out.

Because of the frequent changing of the activated carbon underlayers, the filling-and flushing-out nozzles of the steel filters are subjected to heavy mechanical stress. The pipes, which were originally welded into place, have been replaced by exchangeable ones.

Supervision and controlling of the plants

The pump station and treatment plants are operated and supervised by remote control from a central switchboard. The operation is partly automatic. The distribution of the ozone/air mixture on the gassing containers is done automatically, according to the water throughput.

At present, plants for the automation of the flushing process for the two-layer activated carbon filters are being installed. The flushing process is to be initiated depending on the amount of throughput and on the filter resistance, and will then proceed automatically. Freely programmable controls are planned which can analyze analogous and digital signals and which can be used as a reference input for control purposes. This requires using a process computer.

The computer consists of input and output facilities, a central computer, a central memory unit with a maximum storage volume of 32 K. The computer output is recorded on a page printer which may be used to supervise the programme and to record the operation data. It is also intended for danger warning and recording primary data, so that it will be possible to record all disturbances in the operation of the plant according to their location and time.

In order that the computer will not be blocked excessively in times of disturbances, a line writer is to be installed. Disturbances within the computer up to the periphery are signalled independently. Any disorder in the computer is signalled to a video screen. The computer is designed to take over additional arithmetical-, operational- and automational tasks for all activities within each working group.

Expansion of an activated carbon plant

The activated carbon plant at Holthausen is presently being extended by 12 filters. From a technical point of view, the transport and installation of the filters ought to be of interest. The transport of the steel containers, weighing 30 t and with a diameter of 5 m and a height of 8 m, was made by ship on the Rhine from the manufacturer to the shipyard Reisholz in Düsseldorf. They were then loaded onto a special transporter and carried by road to the building site. The containers were then rolled with tank rollers, as used by army vehicles, via guiding rails to the finished concrete foundations in the pre-fabricated filter hall made of reinforced concrete. This was the first use of such a procedure for a container of this size.

Many experts are of the opinion that a water treatment plant has to be designed individually to fit the circumstances existing in each individual case. This is correct to a certain extent. Nevertheless, the aim should be to standardize the design of treatment plants and treatment steps for drinking water as far as possible. New processes are generally very expensive and not necessarily fully developed. An even greater exchange of experience between the operators of waterworks than has been the case so far would be most useful in this connection.

INVESTIGATIONS OF THE OPTIMIZATION OF PRETREATMENT WHEN USING OZONE

by W. Scheidtmann, Duisburg

Like many other Rhine waterworks, a combined ozone-activated carbon treatment for processing highly loaded bank filtrate is used by the city of Duisburg's waterworks. Similarly, it was shown at Wittlaer at the end of the 1950s that in addition to disinfection of the water, ozone also provided a good pretreatment.

The high consumption of activated carbon caused by the increased pollution of the Rhine was considerably reduced by using ozone, and at the same time the performance of the filter plant, in use since 1957, was improved.

The process of ozone from oxygen, and its injection into the raw water in a closed pressure system, as was used at Wittlaer, have been reported previously (SIMON, 1968). Therefore, only a schematic layout of the Wittlaer procedure is shown in Fig. 1.

Technical grade oxygen is taken from a liquid oxygen storage tank and passed to a 4-tube ozone generator. The ozone/oxygen mixture produced, containing up to 60 g O_3 per m^3 oxygen is pumped,using water-ring pumps,to two washers. Here gas is dissolved, countercurrently, in part of the total flow.

The undissolved gas mixture is returned to the ozone generator via a drying plant. After an increase of pressure the highly concentrated ozone mixture of about 20 g ozone per m^3 of water is conveyed with the raw water by a distributor tray to a mixing and reaction tank which is filled with Raschig rings, similar to the washers.

Fig. 1: Diagram of an ozone plant at the waterworks III in Wittlaer

After a 4-minute retention in the reactor , the water, containing an ozone surplus of about 0.3 mg/l, reaches a two-stage filter plant. The top stage has a multi-layer filter, the lower stage high-grade activated carbon (see Fig. 2).

Fig. 2: Two-stage filter

The investigations of the optimization of flocculation-filtration at the Wittlaer treatment plant have been published (SCHEIDTMANN, 1973) and reported during the discussion meeting of the German Association of Gas and Water Engineers (DVGW) in 1974 at Duisburg.

The following brief report covers further investigations at Wittlaer on the optimization of the oxidation step.

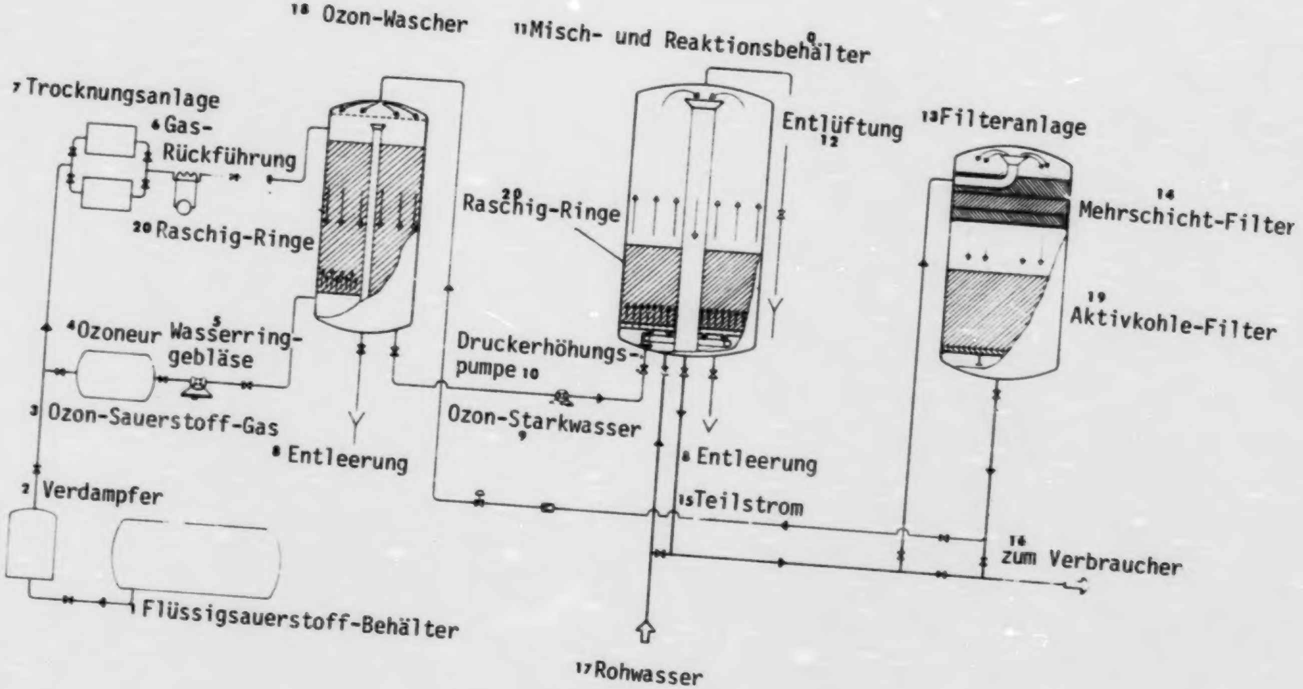

18 Ozon-Wascher
11 Misch- und Reaktionsbehälter
7 Trocknungsanlage
6 Gas-Rückführung
20 Raschig-Ringe
Entlüftung 12
13 Filteranlage
20 Raschig-Ringe
14 Mehrschicht-Filter
19 Aktivkohle-Filter
4 Ozoneur
5 Wasserring-gebläse
Druckerhöhungs-pumpe 10
3 Ozon-Sauerstoff-Gas
Ozon-Starkwasser 9
8 Entleerung
8 Entleerung
2 Verdampfer
15 Teilstrom
16 zum Verbraucher
1 Flüssigsauerstoff-Behälter
17 Rohwasser

Fig. 1 and 2

1 Flüssigsauerstoff-Behälter: liquid oxygen tank
2 Verdampfer: evaporator
3 Ozon-Sauerstoff-Gas: ozone-containing oxygen
4 Ozoneur: ozone generator
5 Wasserringgebläse: water ring blower
6 Gas-Rückführung: gas recycling
7 Trocknungsanlage: drying plant
8 Entleerung: discharge
9 Ozon-Starkwasser: water with high ozone concentration
10 Druckerhöhungspumpe: pump for increase of pressure
11 Misch- und Reaktionsbehälter: mixing and reaction vessel
12 Entlüftung: ventilation
13 Filteranlage: filter plant
14 Mehrschichtfilter: multi-layer filter
15 Teilstrom: recycling fraction
16 zum Verbraucher: to the consumer
17 Rohwasser: raw water
18 Ozon-Wascher: ozone washer; 20 Raschig-Ringe: Raschig rings
19 Aktivkohle-Filter: activated carbon filter

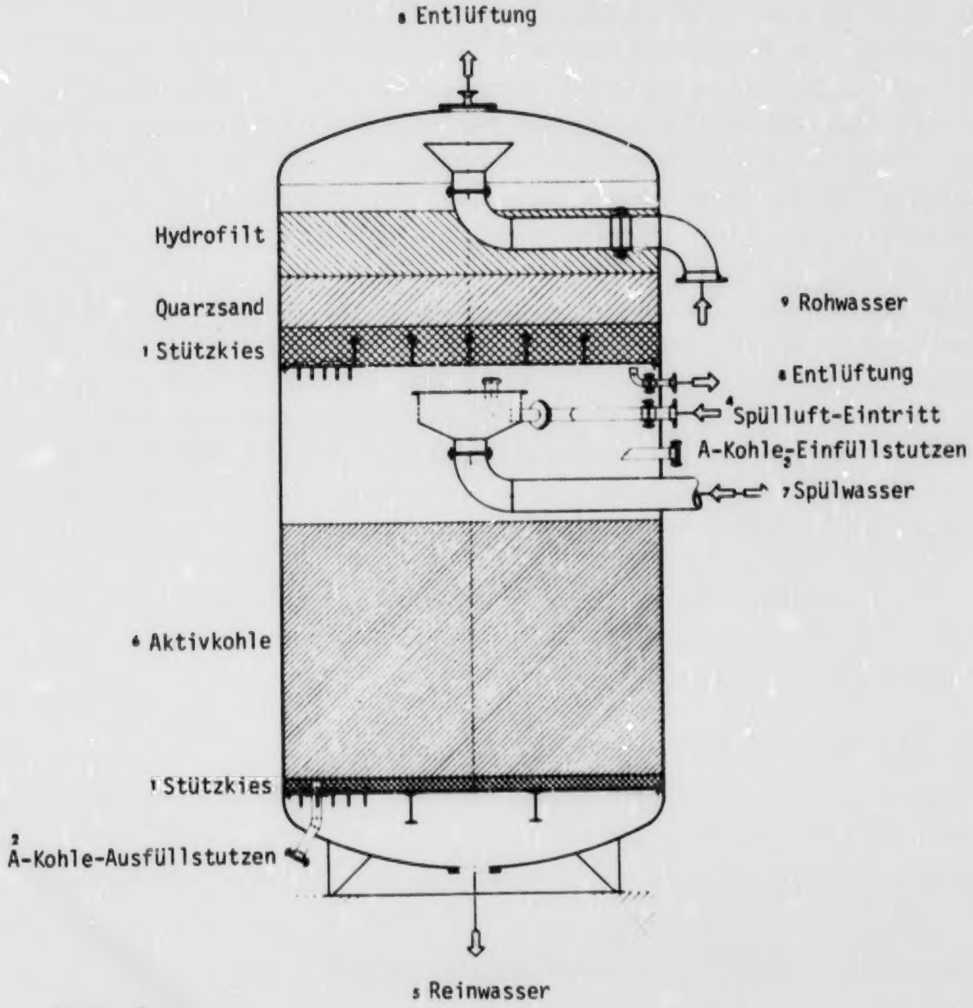

8 Entlüftung
Hydrofilt
Quarzsand
1 Stützkies
9 Rohwasser
8 Entlüftung
4 Spülluft-Eintritt
A-Kohle-3 Einfüllstutzen
7 Spülwasser
6 Aktivkohle
1 Stützkies
2 A-Kohle-Ausfüllstutzen
5 Reinwasser

Fig. 2:

[1] Stützkies: supporting gravel ; [6] Aktivkohle: activated carbon
[2] A-Kohle-Ausfüllstutzen: outlet pipe for activated carbon
[3] A-Kohle-Einfüllstutzen: feeding pipe " " "
[4] Spülluft-Eintritt: inlet for backwash air
[5] Reinwasser: treated water; [7] Spülwasser: backwash water

[8] Entlüftung: Ventilation
[9] Rohwasser: Raw water

After being in operation for some years, it was found that the Raschig rings in the mixing and reaction tanks of the ozone plant, installed in 1966, were becoming increasingly clogged. Clearly, a significant amount of the manganese had precipitated out as pyrolusite. The one advantange of the removal of manganese, and other undesirable components, in the reactors is that they reduce the load on the succeeding multi-layer- and activated carbon filters.

But, as the reactors cannot be backwashed, there are increased pressure losses because of the degree of clogging, which also results in increased maintenance and repair costs. However, if one alters the functioning of the reactors by filling them with filter material instead of Raschig rings, and makes provision for backwashing then the reactor acts simultaneously as a pre-filter, whose filter capacity can be controlled by the adequate addition of ozone.

In line with these considerations, the following test programme was set up in conjunction with the Engler-Bunte-Institute of the University of Karlsruhe:

1) Determination of a suitable filter material.
2) Application of different ozone additions before the reaction filter and the multi-layer filter.
3) Determination of the optimum filter velocities and filter running times.
4) Additional use of flocculants and flocculant aids.

Preliminary tests have shown that the very porous Hydrofilt, which has been in successful use for some time in multi-layer filters, is also suitable for use in a pre-filter. This material yielded the best results with regard to good filter volume effectiveness and running time.

First of all, four different granule sizes, 2.5- 3.5 mm, 3-5 mm, 5-8 mm, 8-10 mm were examined. Plexiglass filters of 150 mm diameter and filter layer height of 1 m were used for the tests; the experimental layout of which is shown in Figure 3.

All four filters were run at a filter velocity of 70 m/h and with an ozone dosage of 2.5 - 3.0 g/m^3 of water.

The 2.5-3.5 mm and 3-5 mm granules were excluded from subsequent tests because the pressure drop increased too rapidly compared with the other granule sizes.

The subsequent tests using 5-8 mm and 8-10 mm granules gave almost the same degree of purification, with the 8-10 mm granules having the lowest rate of increase in pressure drop.

The most significant results with ozone additions before the reaction filter and before the multi-layer filter of 1.5 g/m^3 and 2 g/m^3 are set out in Table 1. It should be noted that with the poorer raw water larger additions of ozone were required.

Running times of at least 8 days should be obtained with the pre-filter and a maximum pressure drop of 5 m. For this reason, only 8-10 mm Hydrofilt granules were used in further tests.

Fig. 3: Reaction filter tests with 4 different granule sizes

Table 1: Reaction- and multi-layer filter tests with ozone addition before and after the reaction filters.

Fig. 4: Layout of the reaction- and multi-layer filter tests with ozone and flocculant dosing

In the next test series aluminium sulphate, ferric chloride and a polyelectrolyte flocculants and flocculant aid were also used. The test layout is shown in Fig. 4.

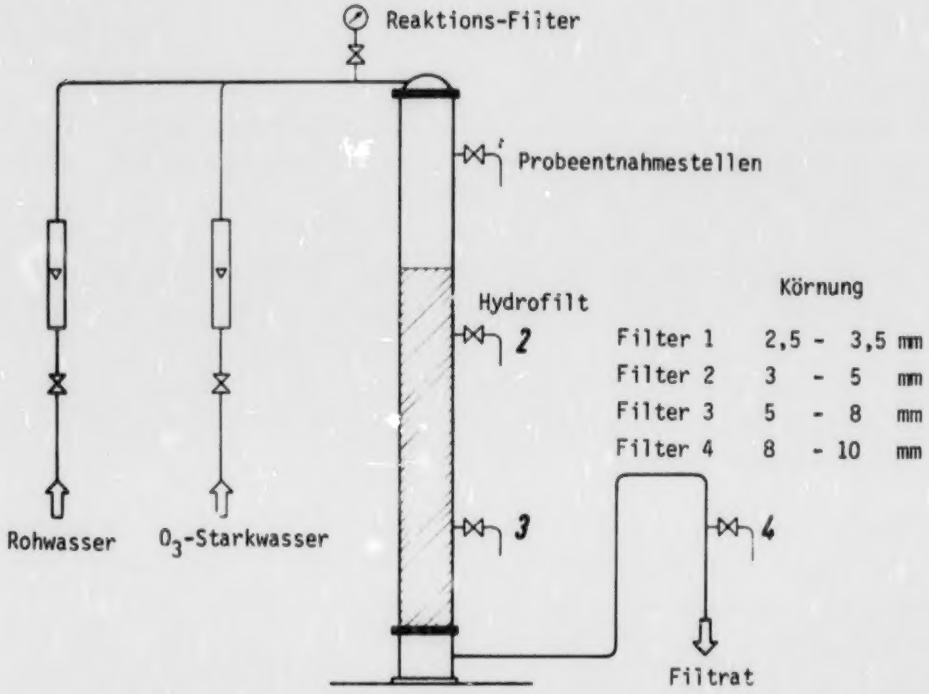

Reaktions-Filter
Probeentnahmestellen
Hydrofilt
2
3
4
Körnung
Filter 1 2,5 - 3,5 mm
Filter 2 3 - 5 mm
Filter 3 5 - 8 mm
Filter 4 8 - 10 mm
Rohwasser
O_3-Starkwasser
Filtrat

Fig. 3

Probeentnahmestellen: sampling points
Körnung: grain size
Rohwasser: raw water
O_3-Starkwasser: water with high O_3 concentration
Reaktions-Filter: reaction filter
Filtrat: filtrate

Table 1: Reaction- and multi-layer filter tests with ozone addition before and after the reaction filters

Filter 1 Reaction Filter filter height 1000 mm Hydrofilt
filter velocity 70 m/h

Filter 2 Multi-Layer Filter
filter height 600 mm Hydrofilt 2.5-3.5 mm
400 mm quartz sand 0.9-1.2 mm
filter velocity 17 m/h

UV = UV extinction (240 nm)

Granulation	Filter 1 5-8mm	Filter 2	Filter 1 5-8mm	Filter 2	Filter 1 8-10mm	Filter 2	Filter 1 8-10mm	Filter 2
Dosage	1,5g O_3/m^3	1,5g O_3/m^3	2,0g O_3/m^3	2,0g O_3/m^3	1,5g O_3/m^3	1,5g O_3/m^3	2,0g O_3/m^3	2,0g O_3/m^3
UV								
Inlet	0,127	0,100	0,135	0,102	0,127	0,102	0,135	0,103
Filtrate	0,100	0,072	0,102	0,077	0,102	0,067	0,103	0,070
Mn								
Inlet	0,90	0,70	1,25	1,10	0,90	0,75	1,25	1,13
Filtrate	0,70	0,01	1,10	0,03	0,75	0,01	1,13	0,03

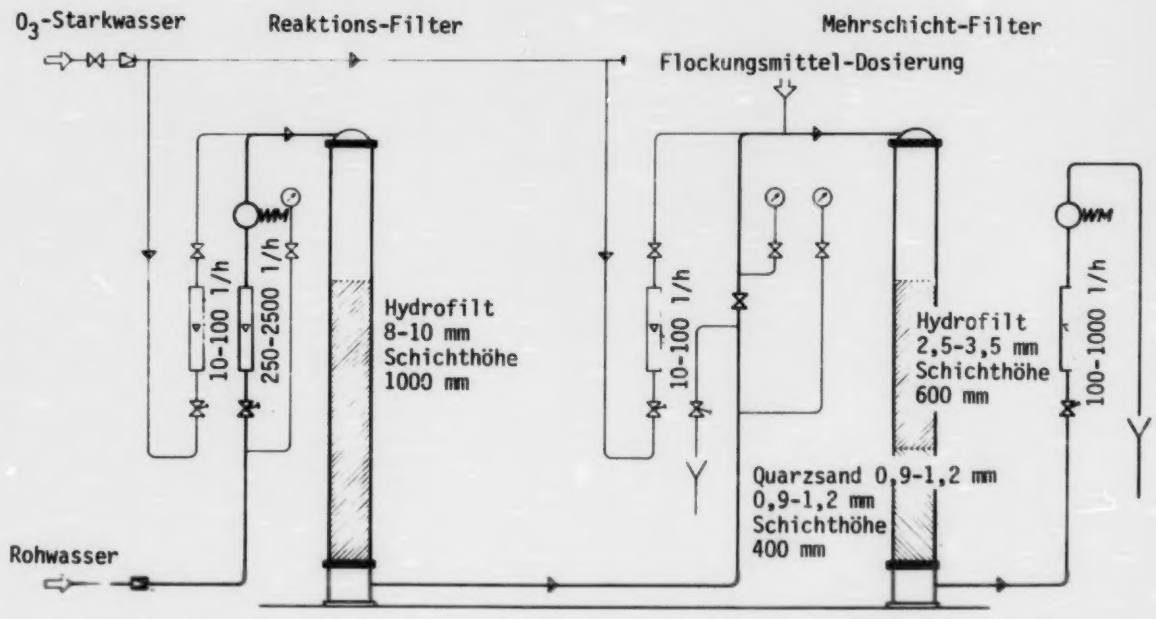

O_3-Starkwasser
Reaktions-Filter
Mehrschicht-Filter
Flockungsmittel-Dosierung
10-100 l/h
250-2500 l/h
Hydrofilt
8-10 mm
Schichthöhe
1000 mm
10-100 l/h
Hydrofilt
2,5-3,5 mm
Schichthöhe
600 mm
100-1000 l/h
Quarzsand 0,9-1,2 mm
0,9-1,2 mm
Schichthöhe
400 mm
Rohwasser

Fig. 4

Probeentnahmestellen: sampling points

Körnung: grain size

Rohwasser: raw water

O_3-Starkwasser: water with high O_3 concentration

Reaktions-Filter: reaction filter

Filtrat: filtrate

Mehrschicht-Filter: multi-layer filter

Flockungsmittel-Dosierung: flocculant dosage

Schichthöhe: filter height

Quarzsand : quartz sand

In order to achieve a more effective treatment, by extending the retention time in the filter, the filter velocity was reduced to 50 m/h.

Different ozone amounts were added with the aim of complete oxidation of the Mn^{2+} in the raw water to Mn^{4+}. This would also result in the removal of part of the dissolved organics in the pre-filter.

To begin, both large and small ozone dosages were added before and after the reaction filter. The velocity in the múlti-layer filter is kept constant at 17 m/h because this velocity is used in industrial filters using activated carbon.

The dosage before and after the filter was then varied.

It was found,satisfactory results were obtained with ozone additions of 1.5 and 2.0 g/m^3 before the reaction filter, and 2 and 3 g/m^3 before the multi-layer filter, as can be seen in Table 2. Flocculants and a small amount of polyelectrolytes were again added to a multi-layer filter, operated in parallel.

From the table one can see that there is a reasonable degree of purification in the reaction filter with an ozone addition of 1.5 g/m^3. A further addition of 2 and 3 g/m^3 ozone before the multi-layer filter resulted in a considerable decrease in the concentration of dissolved organics and manganese. Even more pronounced was the improvement in the degree of purification when, in addition to this, flocculants were added.

Table 2: Reaction- and multi-layer filtration tests with ozone and flocculant dosing

A sufficiently long, baffled, contact path was arranged between the point of flocculant addition and the multi-layer filter, which obviously had a good influence on floc formation.

The final tests were run under the following conditions:

Table 2: Reaction and multi-layer filtration tests with ozone and flocculant dosing

Filter 1 = Reaction Filter filter height 1000 mm Hydrofilt 8-10 mm
filter velocity 50 m/h

Filter 2 = Multi-Layer Filter
filter height 600 mm Hydrofilt 2.5-3.5 mm
400 mm quartz sand 0.9-1.2 mm
filter velocity 17 m/h

Pr.= praestol as flocculant aid, UV=UV extinction (240 nm),
Tr.= turbidity

	Filter 1	Filter 2		Filter 1	Filter 2	
Ozone Dosing	1.5g/m^3	3.0 g/m^3		2.0 g/m^3	2.0 g/m^3	
Flocc. Aid Dosing	-	-	0.5g/m^3 Fe 0.5g/m^3 Al 0.1g/m^3 Pr.	-		0.5 g/m^3 Fe 0.5 g/m^3 Al 0.1 g/m^3 Pr.
UV						
Inlet	0.120	0.091	0.091	0.118	0.090	0.090
Filtrate	0.091	0.060	0.050	0.090	0.066	0.055
Mn						
Inlet	1.03	0.75	0.75	0.92	0.75	0.75
Filtrate	0.75	0.07	0.05	0.75	0.08	0.05
Tr.						
Filtrate	-	0.40	0.30	-	0.50	0.30

1) Ozone addition of 2 g/m^3, each, before the reaction filter and the multi-layer filter.

2) Flocculant addition of 2 g Al/m^3 and 0.1 g $Praestol/m^3$.

3) Contact paths of the same length were used before the multi-layer filter when using both ozone and ozone and flocculant.

4) The velocity in the reaction filter was 50 m/h and in the multi-layer filter 17 m/h.

The most important results of this test series are set out in Table 3.

Table 3: Reaction and multi-layer filtration tests with ozone and flocculant dosing, using a constant contact path.

In conclusion, the following can be said:

The reduction in concentration of dissolved organics, measured by UV extinction, are quite favourable at these ozone additions, in the filtrate from the multi-layer filter. Also, the turbidity data are so good that it can be confidently expected that the following activated carbon will remove the remaining substances in the water, especially the organo-chloro compounds.

A suitable contact path, after the second ozone addition, is also then necessary in those cases where no further addition of flocculant is made. Obviously, this strongly influences the effectiveness of the treatment. The addition of flocculant showed no notable improvement in the test series. However, it may be necessary if the quality of the bank filtrate were to be extremely poor, for instance, after a long drought and lowered water levels in the Rhine. For this reason, an additional flocculation step was not included during the subsequent extention of the treatment plant at Wittlaer.

Table 3: Reaction and multi-layer filtration tests with ozone and flocculant dosing, using a constant contact path

Filter 1 = Reaction Filter filter height: 1000 mm Hydrofilt
8-10 mm
filter velocity: 50 m/h

Filter 2 = Multi-Layer Filter
filter height: 600 mm Hydrofilt
2.5-3.5 mm
400 mm quartz sand
0.9-1.2 mm
filter velocity: 17 m/h
flocculant : Al = aluminum sulphate
Pr = praestol

	Filter 1	Filter 2		Filter 1	Filter 2	
Ozone Dosing	$2 g/m^3$	$2 g/m^3$		$1 g/m^3$	$2 g/m^3$	
Floccul. Aid Dos.	-	-	-	-	-	Al + Pr. $2 g/m^3$ + $0.1 g/m^3$
Contact Path	no	no	yes	no	yes	yes
UV-Ext. (250 nm)						
Inlet	0.085	0.057	0.057	0.102	0.069	0.069
Filtrate	0.057	0.039	0.030	0.069	0.040	0.031
Mn(mg/l)						
Inlet	1.02	0.90	0.90	1.24	0.93	0.93
Filtrate	0.94	0.17	0.04	1.08	0.04	n.n.
Turbidity (JTU)						
Filtrate	6.8	0.60	0.15	7.0	0.14	0.10

Finally, it should be mentioned that the double addition of ozone is of advantage, especially at an increased ammonia content in the bank filtrate. One has then - also at very high NH^{4+} concentrations - sufficient oxygen available for the biological oxidation of the NH^{4+}. Also, it is possible to adjust the oxygen content in the treated water, to a desired value, by a suitable choice of the ozone additions before and after the reaction filter.

The described method of an optimum pretreatment of Rhine bank filtrate provides an important contribution to obtaining a good quality drinking water, even with poor quality rawwater, as is occasionally the case along the lower Rhine.

PRACTICAL EXPERIENCE IN THE USE OF FLOCCULATION FILTRATION CONNECTED IN SERIES TO GRANULAR ACTIVATED CARBON FILTERS

by E. Heymann, Duisburg

Since it has already been described in more detail elsewhere (HEYMANN 1974), the purification process will be discussed only briefly here by means of the flow scheme shown in Fig. 1.

Fig. 1: Flow Scheme, waterworks No. 1

Purpose of the water purification process is the complete removal of undesirable water impurities. Our raw water has virtually no oxygen, consisting almost entirely of bankfiltrate from the river Rhine. The water flows under pipe pressure (6 bar) to the purification plant. The first step of the purification process is the addition of a sodium hypochlorite solution in order to oxidize ammonium ions followed immediately by the addition of a solution of pottassium permanganate and aluminum chloride. The permanganate is intended to oxidize nothing but the iron and manganese salts dissolved in the raw water. The mixture of hydrated iron and manganese oxide floc formed thereby is already capable to adsorb small amounts of organic water impurities. This effect is intensified by the floc formed due to hydrolysis of the aluminium chloride added simultaneously.

In order to stabilize the floc an organic polyelectrolyte is added at the inlet of the two-stage filters. After at least 10 minutes the water reaches the prefilter stage which consists of three layers: activated carbon, anthracite and sand. The flocculation stage is so adjusted that small shear-resistant floc with large surface areas are formed.

Next in flow direction follows a 2 m-layer of granular activated carbon. The brand in use is NORIT ROW 0.8 supra which is rod-shaped and has been reactivated at least four times so far. In contrast to other reports the uniformity of the rods is so poor that they settle in an identical manner after each filter backwash. The average filter rate is 10 m/h. It varies between 5 and 20 m/h.

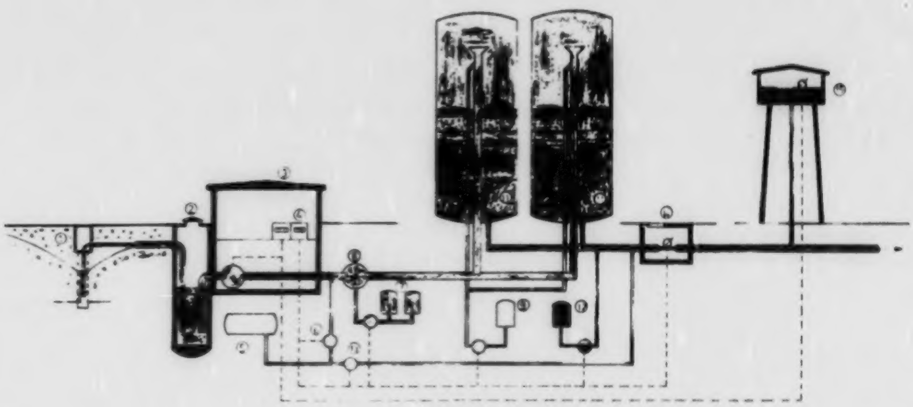


Fig. 1

1) well for bank-filtered water
2) collecting well
3) pumping station
4) automation control
5) sodium hypochlorite
6) break-point chlorination
7) flocculant
8) mixer
9) flocculant aid
10) first filter
11) second filter
12) sodium hydroxide
13) safety chlorination
14) water meter
15) pressure control/distribution system

The purified water is treated with sodium hydroxide for pH control and once more with sodium hypochlorite as disinfectant. The automatically working purification plant has now been in operation for 4 years.

Table 1: Effectiveness of various process steps

	mg C/l	%removal	COD(mg O_2/l)	%removal
1) raw water	2.63	-	9.2	-
2) raw water + 0.45 μ filtered	2.62	-	9.3	-
3) raw water + 2 mg Cl_2/l + 0.45 μ filtered	2.65	-	9.1	-
4) raw water + 2 mg Cl_2/l + 2 mg $KMnO_4$/l (floc in $NaNO_2$ + H_2SO_4 dissolved) + 0.45 μ filtered	2.62	-	9.0	-
5) raw water + 2 mg Cl_2/l + 2 mg $KMnO_4$/l + 0.45 μ filt.	2.45	6.8	8.0	13.0
6) raw water + 2 mg Cl_2/l + 2 mg $KMnO_4$/l + 5 mg Al^{3+}/l + 0.45 μ filtered	1.58	39.9	5.1	44.6
7) raw water + 2 mg Cl_2/l + 2 mg $KMnO_4$/l + 5 mg Al^{3+}/l + 0.45 μ filtered + 20 mg ROW supr.+ 0.45 μ filtered	0.42	84.0	1.3	85.9

Table 1, showing the effect of each individual step of the purification process, clearly demonstrates that, up to step 5, DOC and COD values remain unchanged. This means that without the flocculation effects of the hydrated manganese oxide the COD and DOC values are not influenced by break-point chlorination and addition of potassium permanganate. It should be pointed out that the DOC variation is very low.

Integration of the flocculation efffect by the hydrated manganese oxide into the purification process causes for the first time a pronounced reduction of the DOC values.

Step 6 shows a substantial decrease of DOC- and COD values due to the adsorption by aluminum hydroxide. The 5 mg Al^{3+}/l added are the optimum cost effectiveness. Step 7 shows the effect of the activated carbon. It should be mentioned, however, that the results of steps 6 and 7 could be very different. Not all of the compounds which are adsorbed onto activated carbon can be eliminated by precipitation. Due to the change of the water level of the Rhine the composition of the raw water varies. Because of this, the effect of precipitation can exceed the effect of the activated carbon in the removal of DOC. Thus, it is clearly demonstrated that the precipitation step cannot replace the activated carbon despite of DOC removals exceeding 75 %.

Generally, the process is controlled in such a way that the DOC content of the filter effluent is always below 1 mg/l. The results shown in Table 1 are based on values obtained in the summer of 1975 when the raw water was of good quality.

To understand the meaning of these results with respect to quality and quantity, liquid-liquid extraction followed by GC was used.

The gaschromatograms shown in Figs. 2 to 5 and 7 to 10 demonstrate typical methodical errors resulting from differences in stability and volatility of the organic substances under investigation. For the purpose of this analysis these substances have not been identified.

Fig. 2: Comparison of gaschromatographic test results of pentane extracts

Substantially decreased are number and quantity of non-polar substances extractable with pentane after the precipitation step (Fig. 2). Interestingly, additional peaks occur in the effluent of a freshly filled activated carbon filter. These peaks appear neither after the precipitation step nor after exhaustion of the activated carbon.

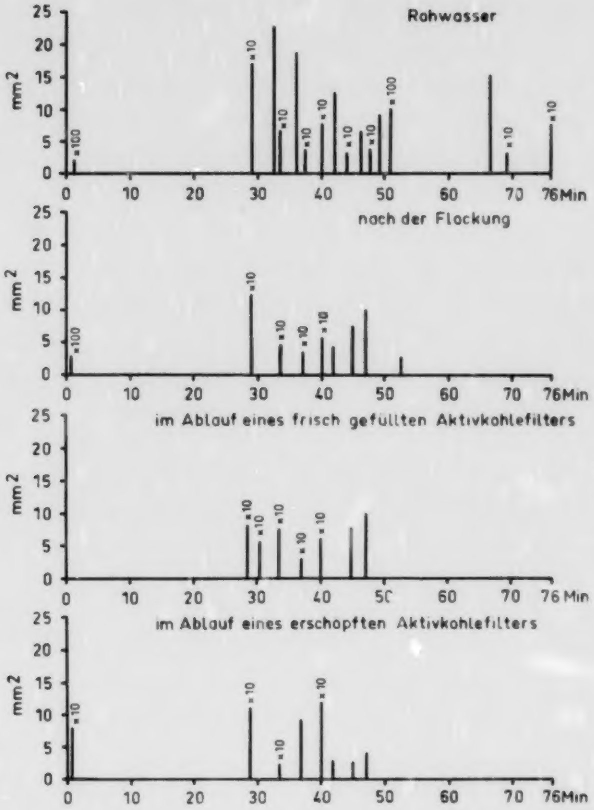


Fig . 2

Rohwasser: raw water
nach der Flockung: after flocculation
im Ablauf eines frisch gefüllten Aktivkohlefilters:
outlet of a filter with fresh activated carbon
im Ablauf eines erschöpften Aktivkohlefilters:
outlet of a filter with exhausted carbon

Fig. 3: Comparison of gaschromatographic test results of i-butanol extracts at pH 1

Fig. 4: Comparison of gaschromatographic test results of i-butanol extracts at pH 4

Fig. 5: Comparison of gaschromatographic test results of i-butanol extracts at pH 9

Figures 3 to 5 show gaschromatograms of the polar organic water impurities. These substances have been extracted from the water with i-butanol at varying pH values. As in the case of non-polar substances, concentration and chromatographic effects can be seen: the effluent of exhausted activated carbon filters shows more and higher peaks than the effluent of the precipitation step or fresh activated carbon.

The effect of the thickness of the carbon layers and the length of the MTZ, and thus the minimum thickness of the carbon bed at a constant filtration rate, can be seen from the diagrams in Fig. 6. The limits of water purification by activated carbon are evident: the water contains impurities which cannot be adsorbed by activated carbon.

Fig. 6: Break-through curves of activated carbon at different layer heights

Another result of our investigations is demonstrated in Figs. 7 to 10. Here the contents of water impurities of pilot filter effluents without preceding precipitation are shown. In each case the activated carbon of the filters was exhausted. The result is that high-boiling non-polar products, which can be degraded biologically, are changed to lower-boiling polar substances in the carbon bed. It can be concluded that biologically-operating carbon filters do not degrade organic substances to CO_2 completely. Apparently, the structure of large amounts of organic compounds is changed only slightly, or not at all.

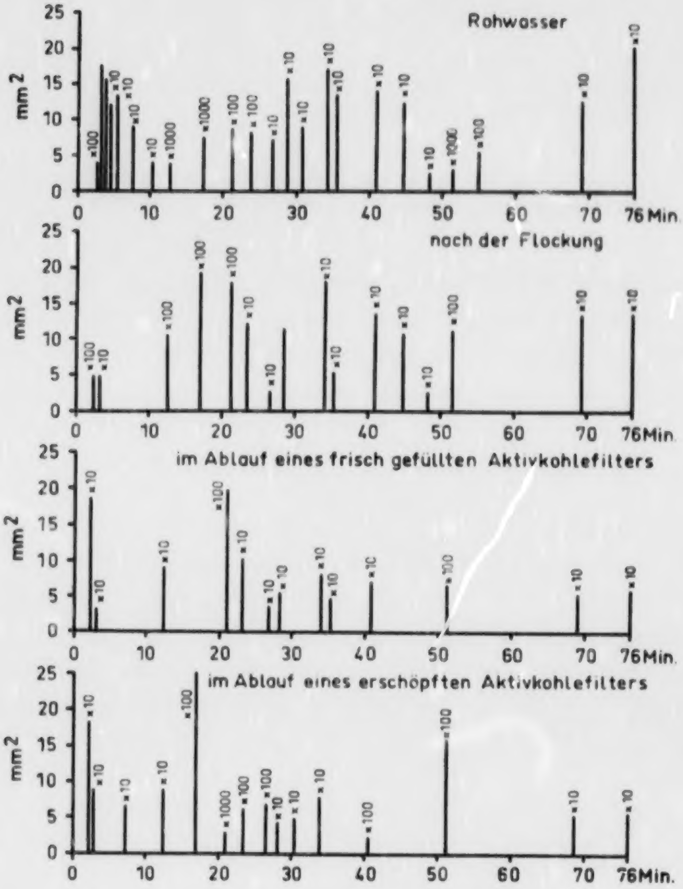


Fig 3

Rohwasser: raw water
nach der Flockung: after flocculation
im Ablauf eines frisch gefüllten Aktivkohlefilters:
outlet of a filter with fresh activated carbon

im Ablauf eines erschöpften Aktivkohlefilters:
outlet of a filter with exhausted carbon

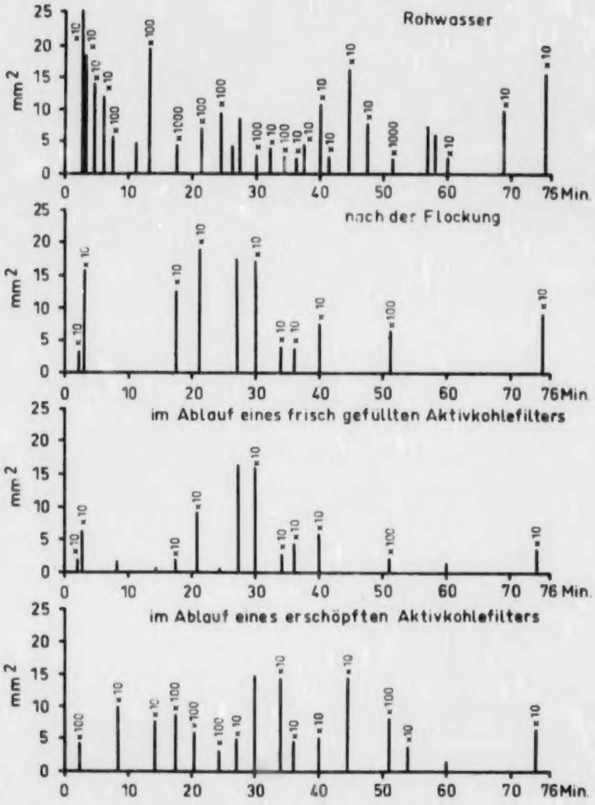


Fig 4

Rohwasser: raw water

nach der Flockung: after flocculation

im Ablauf eines frisch gefüllten Aktivkohlefilters:
outlet of a filter with fresh activated carbon

im Ablauf eines erschöpften Aktivkohlefilters:
outlet of a filter with exhausted carbon

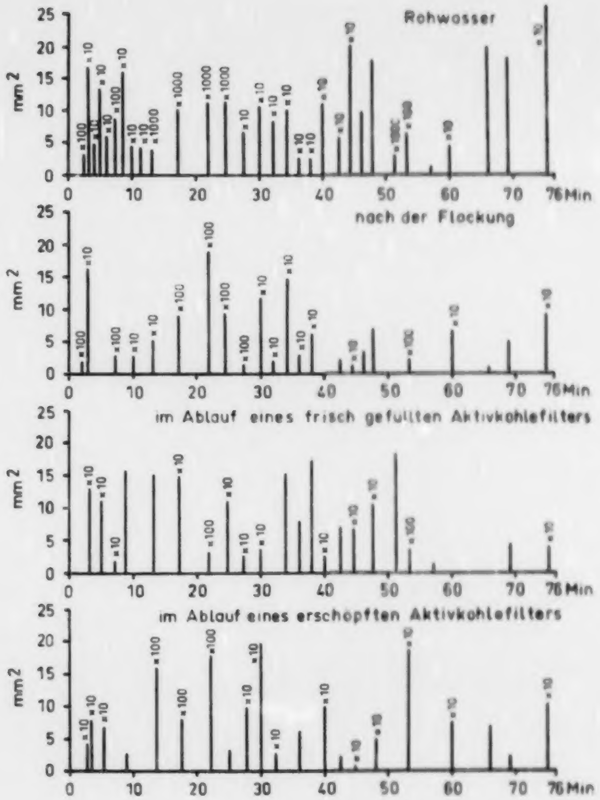


Fig 5

Rohwasser: raw water
nach der Flockung: after flocculation
im Ablauf eines frisch gefüllten Aktivkohlefilters:
   outlet of a filter with fresh activated carbon
im Ablauf eines erschöpften Aktivkohlefilters:
   outlet of a filter with exhausted carbon

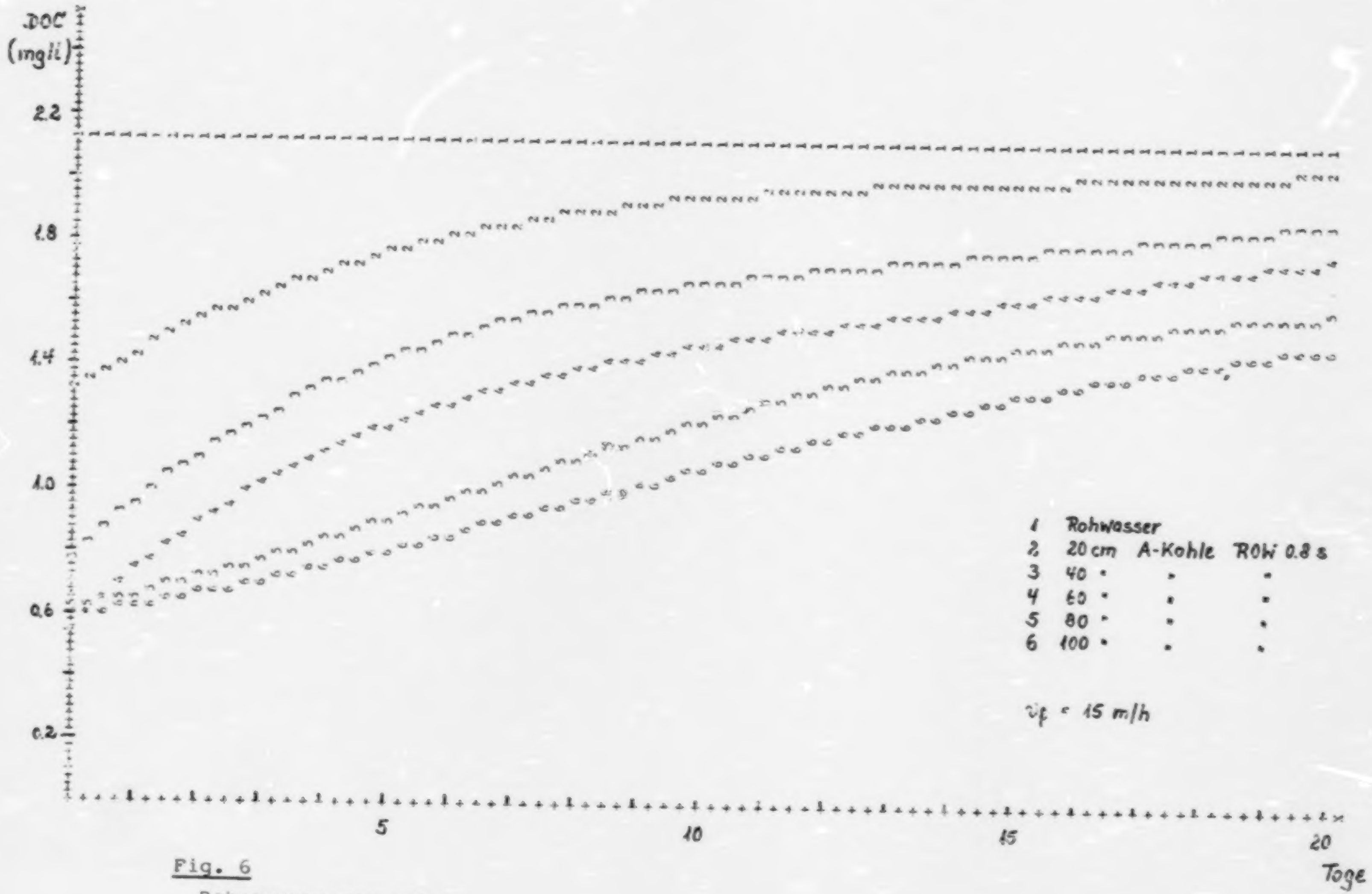


Fig. 6

Rohwasser: raw water

A-Kohle: activated carbon

Tage : days

Fig. 7: Comparison of gaschromatographic test results of pentane extracts

Fig. 8: Comparison of gaschromatographic test results of i-butanol extracts at pH 1

Fig. 9: Comparison of gaschromatographic test results of i-butanol extracts at pH 4

Fig. 10: Comparison of gaschromatographic test results of i-butanol extracts at pH 9

What are the criteria for operating the activated carbon stage of the purification plant?

As a reference figure, the COD value was taken, and a reduction of this value by at least 50 per cent in the activated carbon filter bed was aimed at. Samples taken during one week of each filter led to the results shown in Table 2.

Table 2: Drinking water treatment plant, waterworks No. 1
Loading of activated carbon filters
19th week

Filter	Throughput 1000 m^3	$Q\ \Sigma$ 1000 m^3	Inlet mg/l	Outlet mg/l	Relative Residual Amount	Loading kg
1	18.2	130.1	5.45	1.60	0.293	645.2
2	22.1	69.9	5.50	1.12	0.203	330.0
3	25.5	49.7	5.00	0.70	0.140	208.8
4	33.4	437.0	5.25	3.70	0.704	1326.1
5	29.3	372.8	5.45	3.70	0.678	1073.2

Table 3 shows the likely life span of a filter, computed from values obtained from each filter.

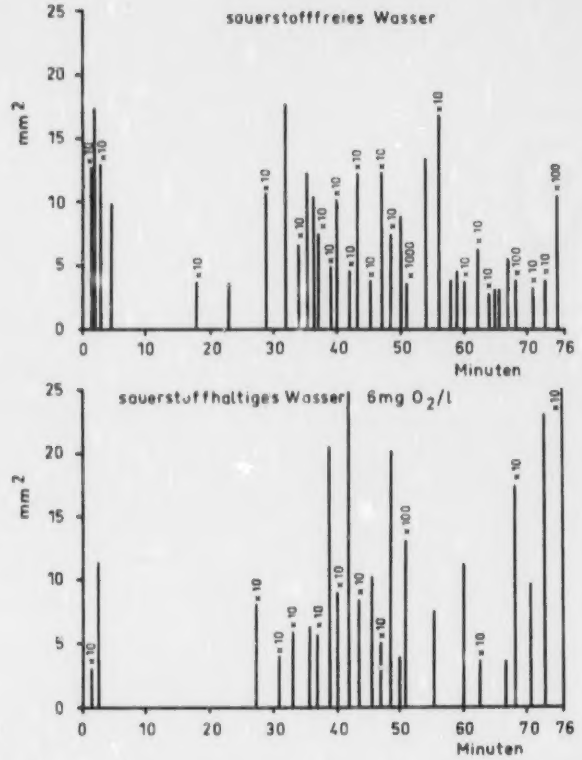
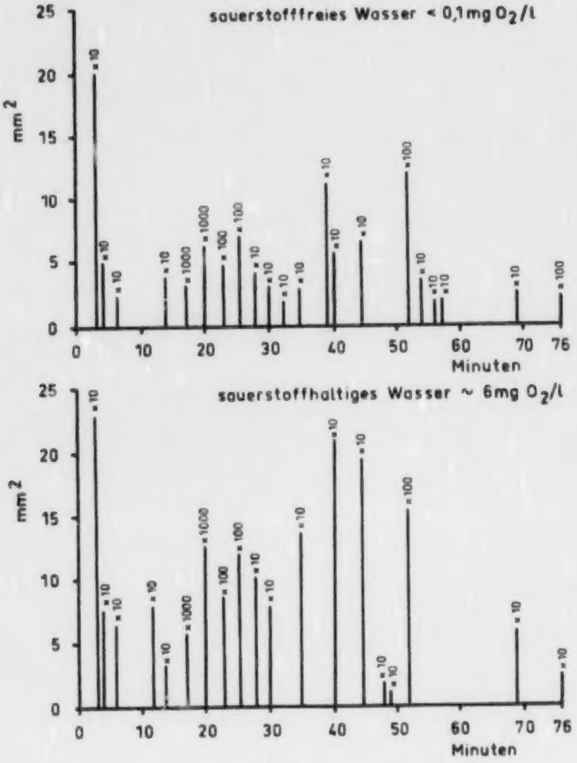


Fig . 7

sauerstofffreies Wasser: water containing no oxygen
sauerstoffhaltiges Wasser: water containing oxygen
Minuten: minutes


sauerstofffreies Wasser < 0,1 mg O_2/l

sauerstoffhaltiges Wasser ~ 6 mg O_2/l

Fig 8

sauerstofffreies Wasser: water containing no oxygen
sauerstoffhaltiges Wasser: water containing oxygen
Minuten: minutes

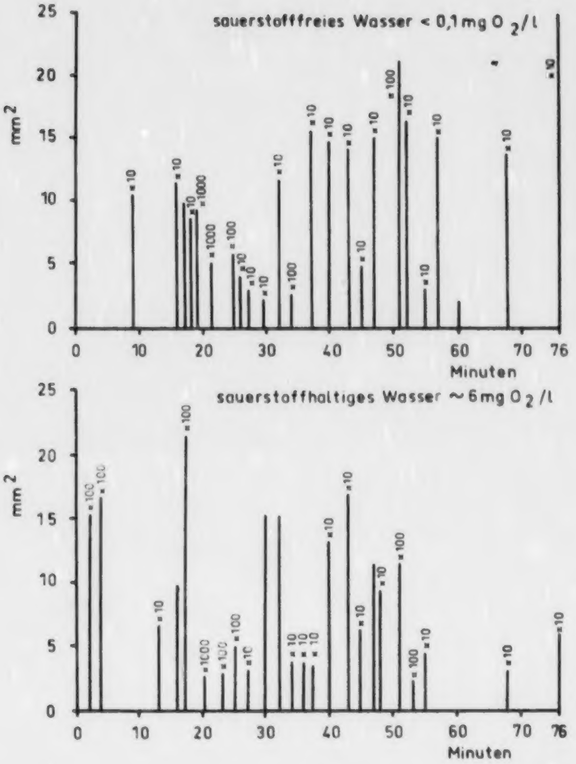


Fig 9

sauerstofffreies Wasser: water containing no oxygen
sauerstoffhaltiges Wasser: water containing oxygen
Minuten: minutes

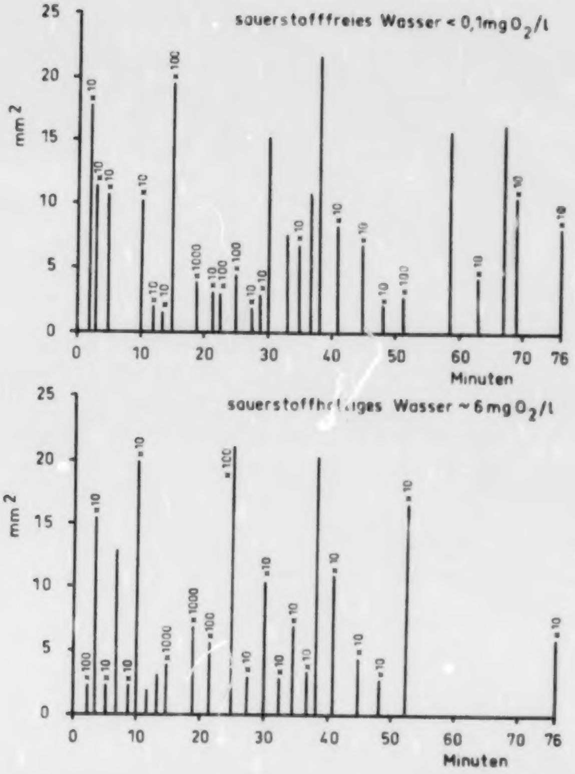


Fig 10

sauerstofffreies Wasser: water containing no oxygen
sauerstoffhaltiges Wasser: water containing oxygen
Minuten: minutes

Table 3: Drinking-Water Treatment Plant, waterworks No. 1
Running time of activated carbon filter No. 1
Calculated Data

Running time (weeks)		Loading (kg)
17	shortest running time	1198
22	medium running time	1530
27	longest running time	1863

The filter efficiency will be obtained with a statistical certainty of 99 per cent

Starting date: 12th week

Assumed end
of filter run: 34th week

USE OF ACTIVATED CARBON IN THE TREATMENT OF LAKE WATER

Maarten Schalekamp, Zurich

General Discussion

First it is necessary to answer the question, why the lake waterworks in Switzerland use the activated carbon filtration method. There are several reasons for this:

For example, the oil-pipeline Genoa-Ingolstadt was laid directly adjacent to the lake of Constance and its surroundings. The best possible safety precautions were observed during the construction, and for the subsequent operation, since the possibility of a pipe break must be taken into account. The results of such a break occurring in a drinking water storage basin of this sort could be disastrous. As a result of efforts taken by several water works, the Energia Nationale Italiana (ENI) was willing to finance the costs of building an ozone- or activated carbon filtration system, for all the works lying within the danger area. In this manner, water contaminated by slight amounts of oil can be purified into drinking water.

Another reason was the phenol spill in the cities of St.Gallen (1957) and Zurich (1967). During these times, large areas of the respective drinking water supplies were highly contaminated and the occurrence of odours and flavours disturbed the area.

These two reasons were the determining factors which led to the installation of an activated carbon filtration system for the water works of the city of St.Gallen, which lie at the Lake of Constance. The phenol spill which occurred in Zurich had such heavy consequences that sufficient impetus was provided for the construction of an additional activated carbon filtration step in the treatment plants of Lengg and Moos.

For most of the other lake water works in Switzerland, however, the sudden appearance of the floating mussel "Dreissena Polymorpha Pallas" (DPP) was the main reason to use the activated carbon filtration system in their lake water works - namely, for the dechlorination.

The consumption of energy, i.e. the use of oil and gasoline, increased six fold during the past few years. Therefore, the organic load of the rivers increased also. K. and G.Grob reported that many organic substances are found on the surface waters but are almost completely absent in pure well water (Fig.1). Investigations carried out in the laboratories of the Zurich water supply confirmed this condition. It is the duty of every water supply to ensure that the quality of the drinking water derived from surface water is in no way inferior to the unobjectionable quality of water found in well - and ground water, particularly with respect to the load of organic substances. Therefore, the conditioning of surface water with activated carbon filtration can no longer be omitted today in Switzerland.

Dechlorination Efficiency of Activated Carbon

Several waterworks in Switzerland use chlorine to prevent the DPP from attacking the raw water pipelines. The chlorine is then removed through activated carbon filtration. Experiments have shown that a concentration of 1 mg/l remains, e.g., upon addition of 1.5 mg/l Cl_2 into the raw water catchment installation, which is 100% effective in eliminating DPP larvae after 11 days (Fig.2).

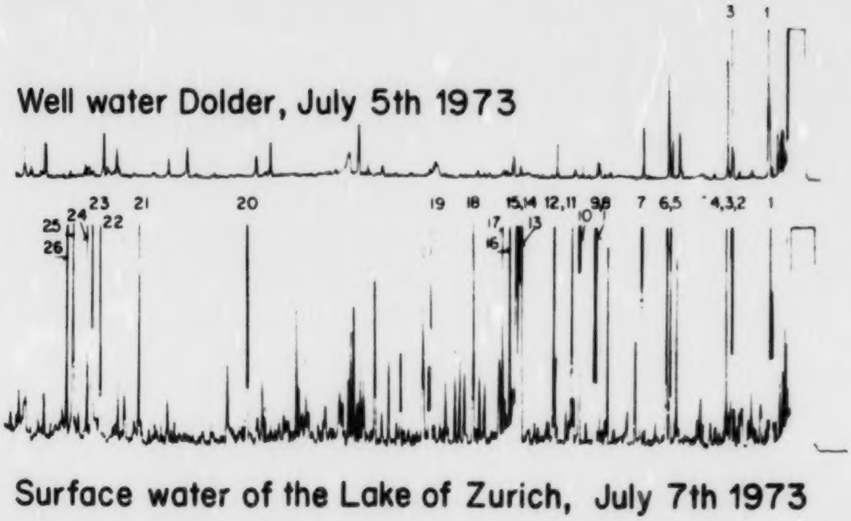


Fig. 1 Organic substances in well- and Zurich Lake water (based on K. and G. Grob)

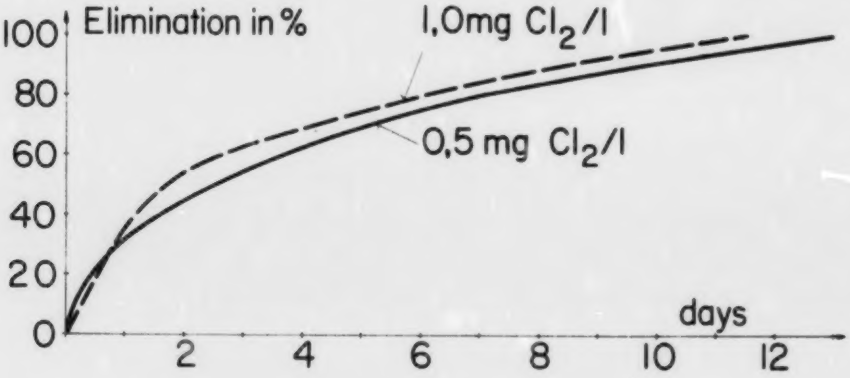


Fig. 2 Elimination of Lake of Constance-DDP-larvae in raw water from the Lake of Zurich using 0.5 and 1.0 mg of Cl_2 per liter as a function of time (based on Dr Siessegger)

This amount of chlorine is sufficient since it has been shown that the larvae are retained in the rapid filter for up to 15 days. As the normal treatment requires less than 1.5 mg/l chlorine, investigations were undertaken to determine if an effective killing of the DPP larvae could be attained with a residual chlorine concentration of 0.5 mg/l, e.g., with a feed concentration of 0.8-1.0 mg/l at the catchment point on the lake. With this dose (Fig. 2), 13-14 days are required to eliminate the DPP larvae. This value lies on the tolerance limit, but may be considered as acceptable. Furthermore, the results obtained by London's water-works showed that a residual concentration of 0.5 mg/l is sufficient. Here in Switzerland, a residual chlorine concentration of only 0.05 mg/l drinking water is permitted, the surplus chlorine must be removed from the water.
Although neutralization with thiosulfate could be considered, activated carbon is used instead as a safety measure by the lake water treatment works. The activated carbon is applied either as a second upper layer in the rapid filters, as a 5-10 cm thick layer above the sand in the slow filters, or as a second top layer again in activated carbon filters.

In order to select the most applicable type, dechlorination experiments were carried out with different activated carbons. These were done for the velocities of the slow - as well as for the rapid filters. With the exception of Hydraffin LW and Pittsburgh 200, all the other carbon types were suitable for the slow filters, such as Norit PKST, Norit 07, Sutcliffe, and Hydraffin LW extra. For the rapid filters, however, the activated carbons of Hydraffin LW extra, Sutcliffe, Norit 07, and Pittsburgh 200 were most suitable (Fig.3). As the effectiveness of dechlorination decreases with time, experiments with different activated carbons were carried out lasting for several months using different velocities (Fig.4,5,6). It is interesting to note how the decrease in efficiency of dechlorination appears for

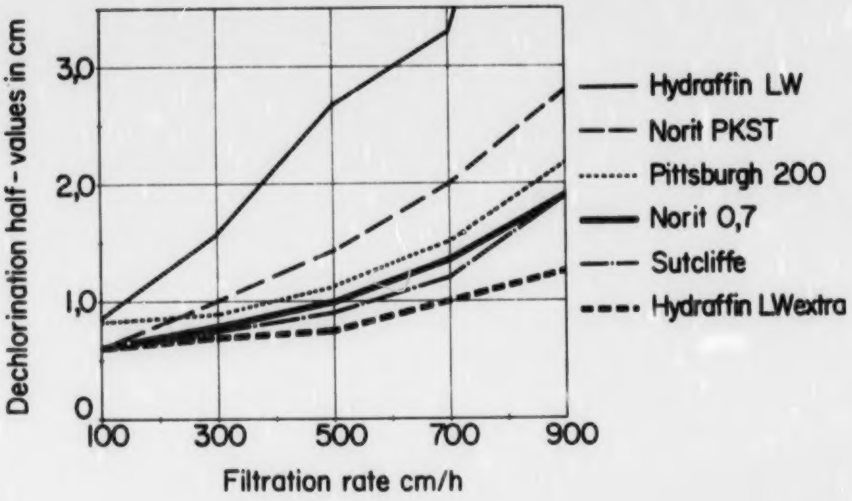


Fig. 3 Dechlorination half-values of various activated carbon types at different filtration rates

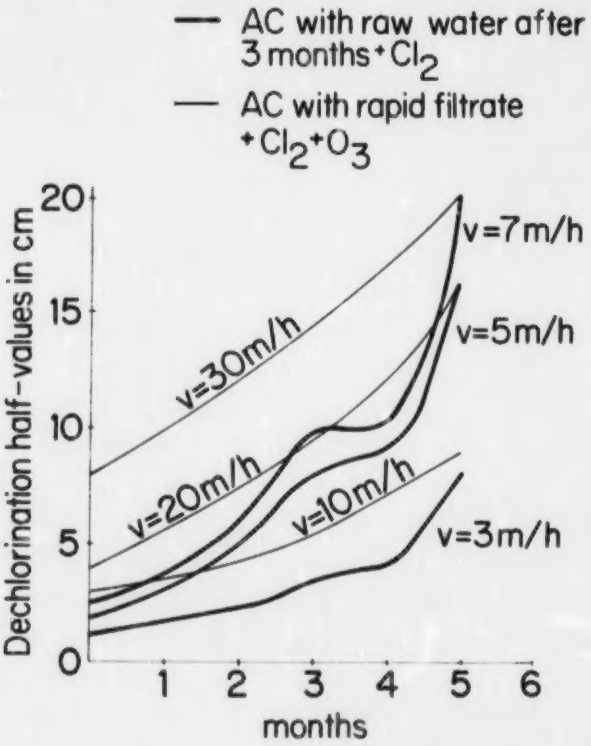


Fig. 4 Decrease in dechlorination efficiency of Norit 07 activated carbon per month at different rates

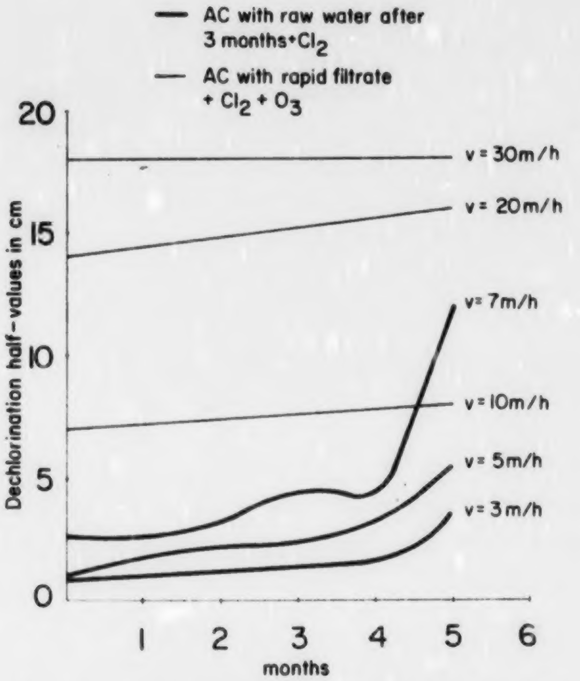


Fig. 5 Decrease in dechlorination efficiency of Lurgi LW Extra activated carbon per month at different rates

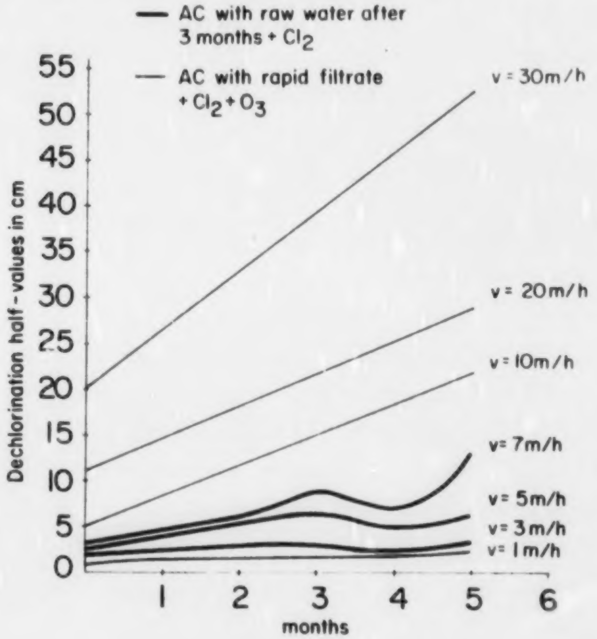


Fig. 6 Decrease in dechlorination efficiency of Norit PKST activated carbon per month at different rates

the activated carbons conveying either raw water or rapid filtrate. As can be seen from Fig. 7, the best results are obtained with Pittsburgh 400, Lurgi LW extra, and Norit 07. A further result from these studies was the dependence of dechlorination upon the grain size of the activated carbon, namely, the smaller the grain size, the higher the efficiency.

Double-layer Rapid - and Slow-filters with activated carbon (AC)

Additional experiments were carried out with one-layer rapid filters and double-layer rapid filters with activated carbon. The double -layer filters consisted of the following materials:

Filter 14 (Fig.8): 60 cm quartz sand, 20 cm AK Norit PKST;
Filter 16: 40 cm quartz sand, 40 cm AK Norit PKST;
Filter 18: 60 cm quartz sand, 20 cm AK Norit 07;
Filter 20 (Fig.9): 60 cm quartz sand, 20 cm Lurgi Hydraffin LW extra.

These double-layer filters were subsequently compared with a one-layer filter filled only with 80 cm quartz sand. The purification effect of the double-layer AC filters was somewhat better than that for the single-layer filter.

The operating time for the double-layer AC filters, however, can be considered as exceptionally efficient (Fig. 10). We must mention though, that the contamination level of the raw water was relatively low during the experimental period, so much longer operating times than normal were possible. While the one-layer filter required backwashing three times during the 25 day interval, this procedure was necessary only once for the double-layer filter with Lurgi-AC. The pressure loss of the double-layer filter was increased with 40 cm PKST - carbon by 30 cm, with 20 cm PKST by 34 cm, and with Norit 07

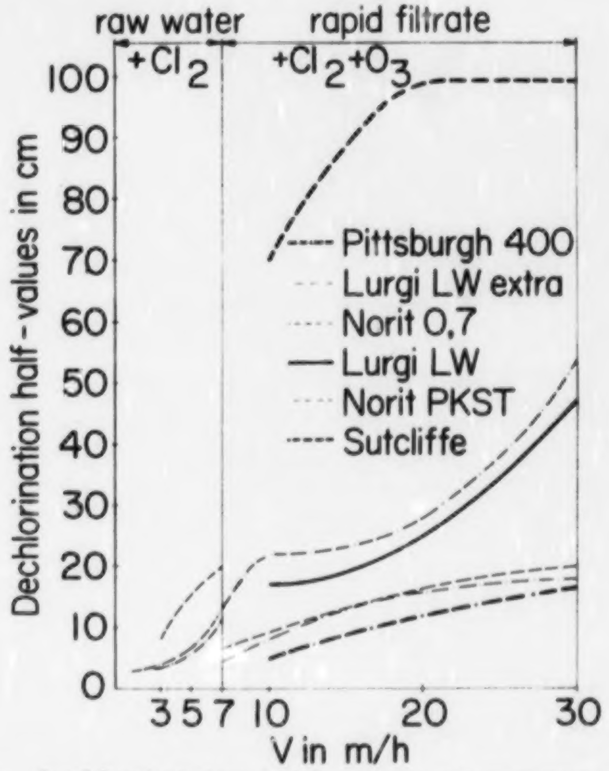


Fig. 7 Dechlorination half values of various types of activated carbon after 5 months at different rates

Fig. 8 Two-layer rapid filter no. 14 with 60 cm of quartz sand (0.4 - 1.0 mm) and 20 cm of Norit PKST activated carbon (0.5 - 2.5 mm)

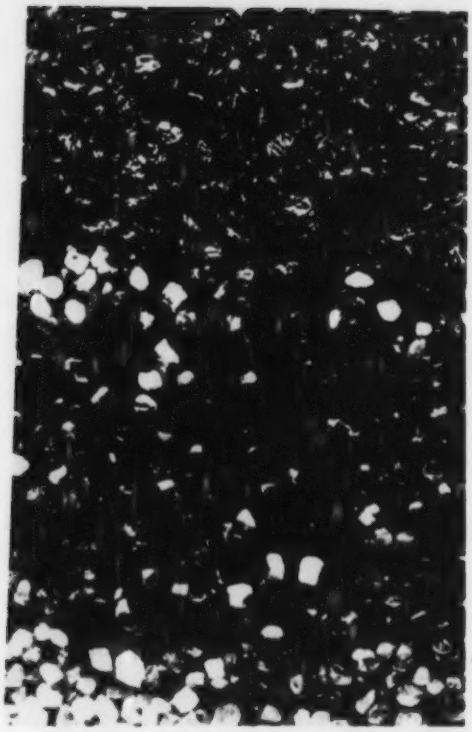


Fig. 9 Two-layer rapid filter no. 20 with 60 cm of quartz sand (0.4 - 1.0 mm) and 20 cm of Lurgi LW Extra Hydrafin activated carbon

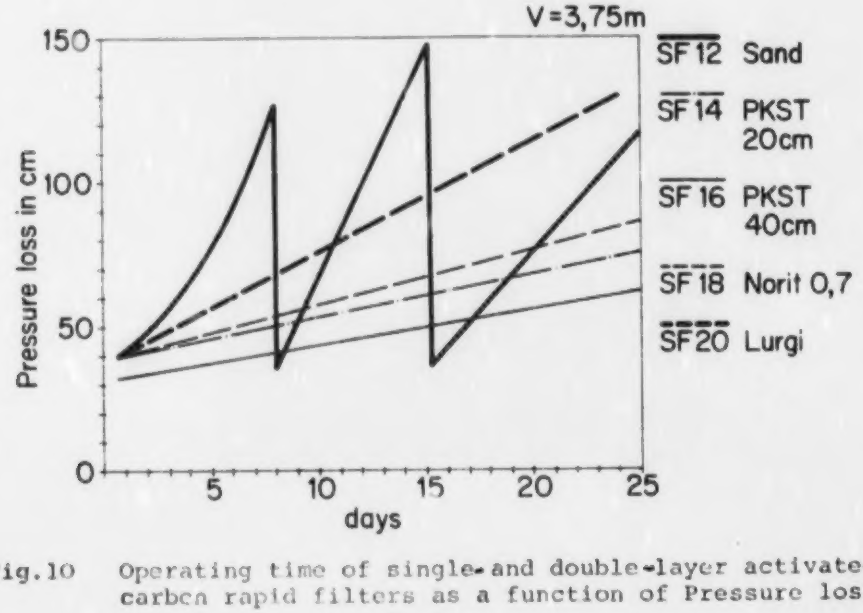


Fig.10 Operating time of single- and double-layer activated carbon rapid filters as a function of Pressure loss

by 46 cm. This increase for the double-layer filter appeared to be primarily due to the presence of the activated carbon layer (Fig.11). The longer or shorter operating time for the double-layer filter is, of course, also dependent upon the grain size of the AC. Following intensive air rinsing, it was possible to rigorously separate the quartz sand and the AC with a back-wash water velocity of only 15m/h.

Most of the lake water-works on the Lake of Zurich impregnate their rapid filters with activated carbon for the purpose of dechlorination. At the water supply for Zurich, the dechlorination was carried out with the slow filter until the completion of the AC filter, which covered the original filter with an AC layer of about 10 cm (Fig.12). It was seen that the operating times were at least five times better than with the one-layer slow filters due to this modification (Fig.13).

A new cleaning process was developed (Fig.14) which made it no longer necessary to remove the AC during the rinsing process. This is a big advantage since the slow filters no longer need to be closed down.

The top layer of the slow filter is backwashed with water, through nozzles which penetrate 20 cm into the AC layer and sand surface. The polluted water is then channelled into the sewage recycling system. This newly developed machine can clean an area of 1000 m^2 within 30-40 hours. The operation requires only one man.

4. The Removal of Organic Substances by the Ac filter

According to K. and G.Grob, at least 186 kinds of organic substances are found in the Lake of Zurich. The ones with the highest concentrations are:

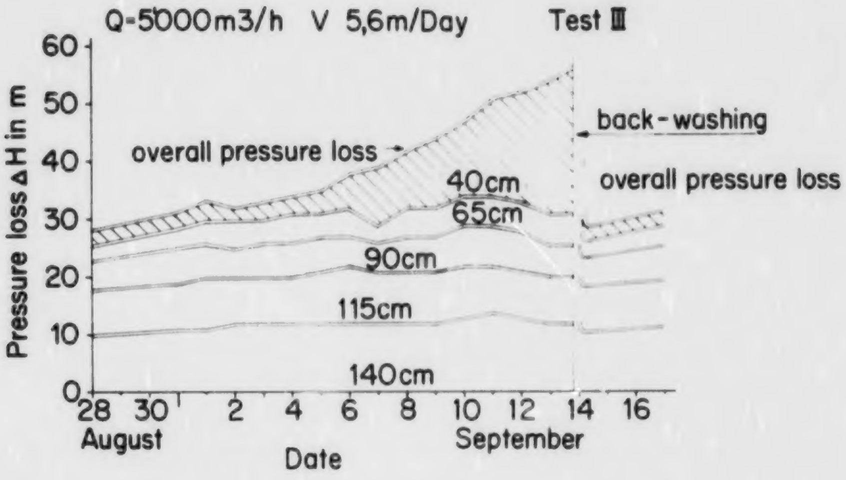


Fig.11 Pressure loss in each layer of a double-layer activated carbon rapid filter

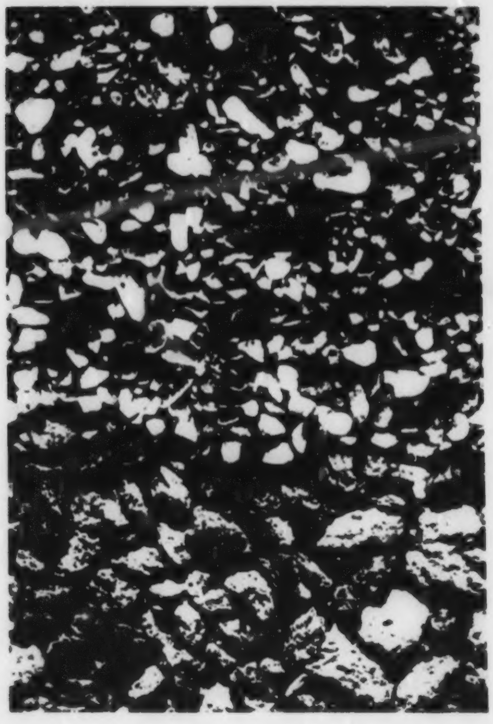


Fig.12 Double-layer slow filter using river sand and 10 cm of Norit PKST activated carbon (0.5 - 2.5 cm)

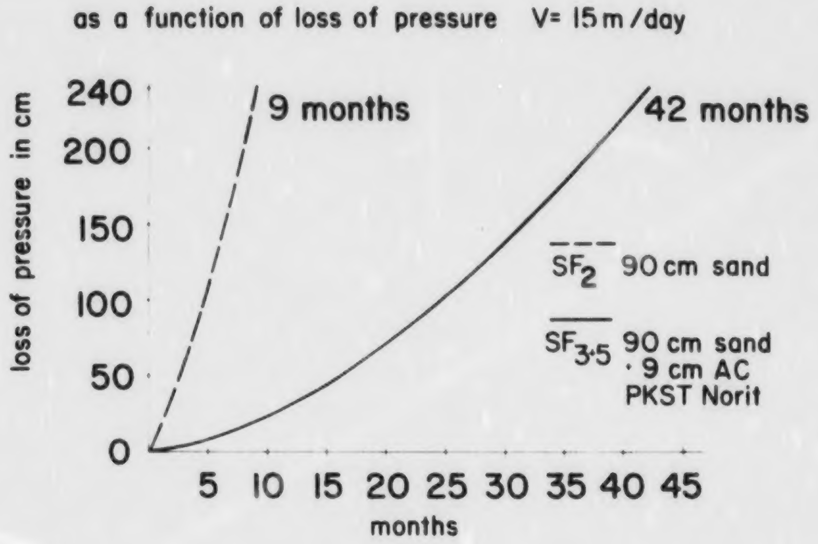


Fig.13 Operating time of single-and double-layer slow filters

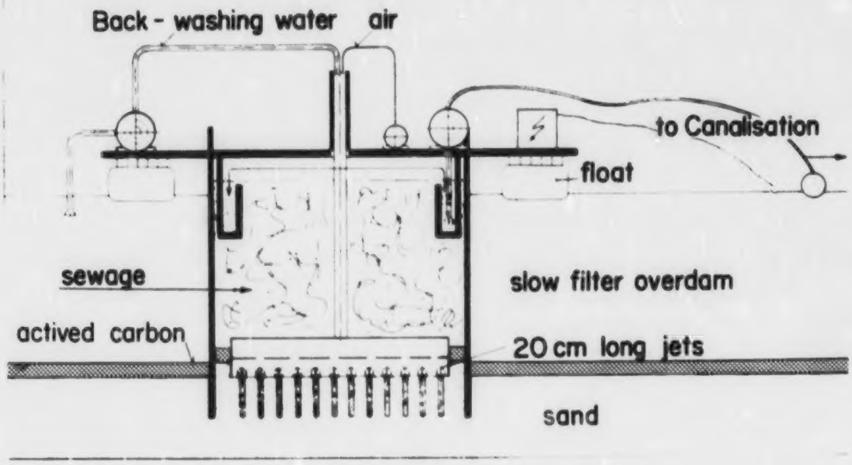

Back - washing water
air
to Canalisation
float
sewage
slow filter overdam
actived carbon
20 cm long jets
sand

Fig.14 Slow filter cleaning machine

1. benzene
2. tetrachloroethane
3. toluene
4. dimethyldisulfide
5. 1.4-dimethylbenzene
6. 1.3- " " "
7. 1.2- " " "
8. 4-ethyltoluene
9. 3-ethyltoluene
10. cineol
11. 2-ethyltoluene
12. 1.2.4-trimethylbenzene
13. dimethyltrisulfide
14. propyltoluene
15. 1.2.3-trimethylbenzene
16. isobutylbenzene
17. dimethylethylbenzene
18. methylisopropylbenzene
19. 1.2.4.5-tetramethylbenzene
20. alkane C_{15}
21. molecular weight 182
22. dimethylnaphthalene
23. alkane C_{17}
24. diphenyl
25. alkane C_{17}
26. diphenylether

From Fig.15 can be seen the amount of organic substances which can be removed from water by 9g of AC. Experiments in Zurich showed that up to 80g of organic substances can be removed from water per kg of AC. These substances are labelled as DMF-extract (DMF=dimethylformamide).

Several types of AC were investigated in Zurich with regard to the removal of organic substances. The order concerning the types of AC tested and the amount of removed organic substances from the raw water of the Lake of Zurich are as follows:

Experiment 1 -Duration 9 months		Experiment 2 -Duration 3 months	
Pittsburgh 400	61 g/kg	Pittsburgh 400	61 g/kg
Norit PKST	41 g/kg	Lurgi LS-Supra	49 g/kg
Lurgi LS-Supra	34 g/kg	PKST	41 g/kg
Lurgi LW	28 g/kg	Pittsburgh 300	38 g/kg
Norit 07	21 g/kg	Norit 08	34 g/kg
		Norit 07	28 g/kg
		Zetclef	26 g/kg

Fig.15

Organic residue from 9 grams of Pittsburgh activated carbon

The best ACs, which additionally demonstrated good reactivation, were Pittsburgh 400, Lurgi LS-Supra, Pittsburgh 300 and Norit 08. The new carbon ROW 08 Supra from Norit was tested and compared with the best suitable carbon, the Pittsburgh 400. Experiments in larger plants already confirmed after one month that it was equal to the Pittsburgh 400. This was further substantiated by longer-termed examinations (Fig.16).
The carbon Pittsburgh 400, was later on used in the AC filtration process of the Lengg lake water-works, while the ROW 08 found its application in the works "Moos". After a two-month operating period in the lake water-works of Lengg a load of 37 g/kg was determined
for the Pittsburgh 400 carbon. In the beginning, the new carbon showed a load of 4g/kg (DMF-extract).
But the capacity increased already after 3 months operating time to 63.5 g and attained the highest capacity with 68.5 g/kg after seven months (Fig.17). Unfortunately, the top as well as the lowest layer showed an equal capacity after seven months. Theoretically the AC had to be changed. But the efficiency with regard to the reduction of organic substances was still as good as at the beginning, as dissolved organic carbon (DOC) and UV proved (Fig.18 and 19).
Even if the AC is completely loaded, as the parameter DMF shows, the efficiency still practically corresponds to the value of new carbon. This could be a result of the biological processes at the AC filter. The exchange of the carbons takes place, therefore, only when the DOC and UV reduction-values fall under a certain limit.

The slow filter in the lake water-works "Moos" was fitted with a 5 cm layer of the AC PKST. The new carbon showed a load of 5g/kg at the beginning. After three years, the load was 29.2 g/kg (Fig.20). The efficiency of

	DMF extract g/kg AC			DMF extract extinction at 300 nm d = 1 cm		
	total load	new	effective load	total load	new	effective load
ROW 0,8 supra	5,5	1,6	3,9	0,062	0,044	0,018
ROW 0,8 supra M	4,1	1,6	2,5	0,093	0,044	0,049
Pittsburgh F400	6,1	3,7	2,4	0,121	0,109	0,012

Fig.16 Test 3; Load comparison of various activated carbons, 34 days (1974), Water throughput of 4,5 m^3 per kilogram of carbon

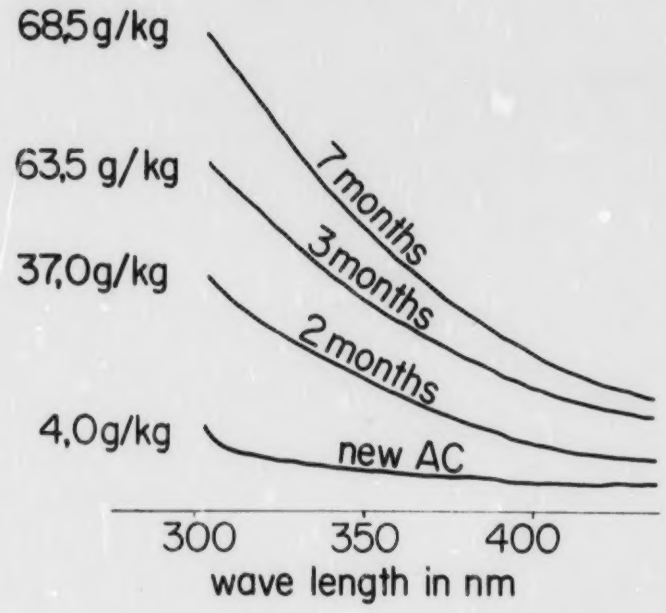


Fig.17 Activated carbon load:new carbon as well as after 2,3 and 7 months of operation; UV-spectra of DMF extracts

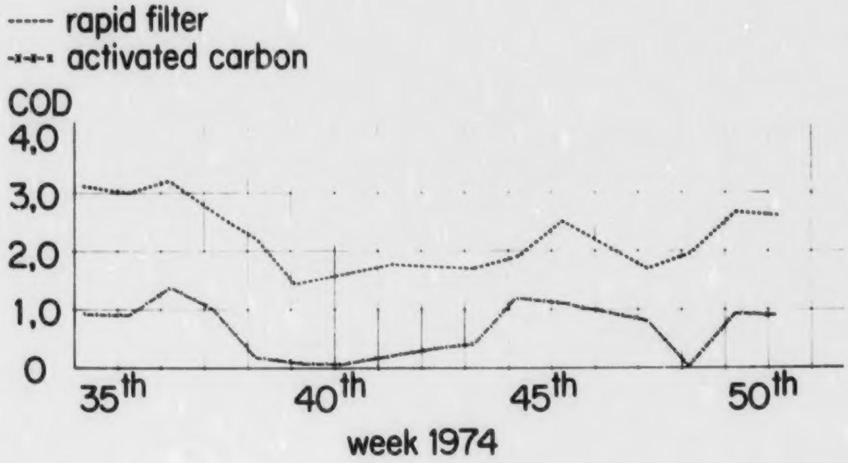


Fig.18 Lengg lakewaterworks; COD in mg O_2/l in rapid and activated carbon filtrate

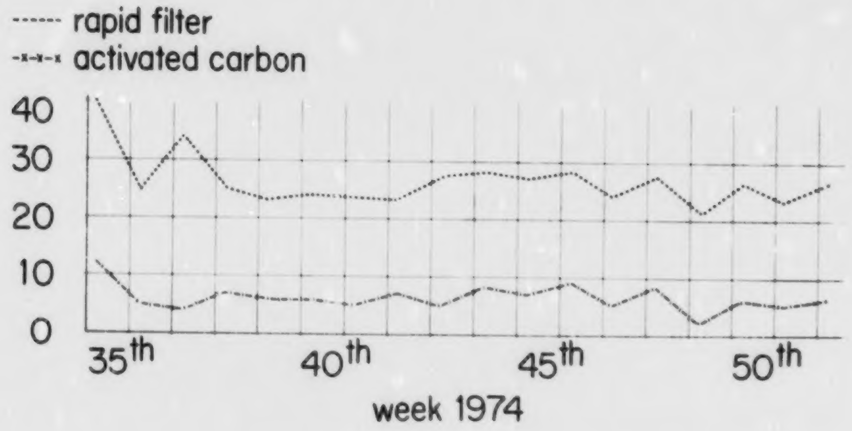


Fig.19 Lengg lakewaterworks; UV = 254nm; d = 1 cm. 10^{-3}

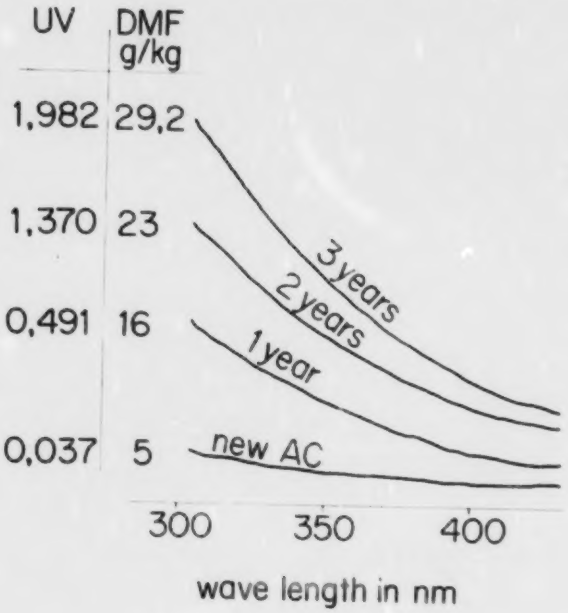


Fig.20 Activated carbon load from the slow filter; new carbon after a filter operating time of 1,2 and 3 years; UV-spectra of the DMF extracts

this carbon with respect to the removal of organic substances, for example, COD (chemical oxygen demand) was equally good for three years. (Fig.21)

Therefore the construction of a separate AC filter, for the recharge of ground water at the ground water-works "Hardhof" for the water supply of Zurich, can be renounced after the recharge basins showed an equal efficiency when they were fed with AC. In addition, **the operating time of the recharge basins increases by five times.**

Reinfection

It is known that AC leads to reinfection. Experiments in pilot plants proved this in Zurich. Fig.22 shows that the highest bacterial count was found for the Norit PKST carbons at the beginning. The number of germs of the Pittsburgh 400 was about half that for Norit PKST and the value of Lurgi LS-Supra was even a little bit lower. The Sutcliffe-carbon showed the best results. At the end, practically the counts for all of the mentioned AC types were equally high except for the value of the Sutcliffe-carbon. Its value was only a third of the others, namely, 343 germs per cubic centimeter.

It is obvious that there is a close relationship between the reduction of the organic substances and the reinfection, specially true for the AC PKST. At the beginning it was the most effective with respect to the removal of organic substances, but it showed also the highest reinfection number for the same time. As experiment 2(Fig.23) strikingly shows, all monthly backwashing carbon types exhibit a bacterial count of 5 digits already after an operating time of one month. The weekly backwashing carbons Sutcliffe 206A and Norit PKST showed only a number of four digits, and already

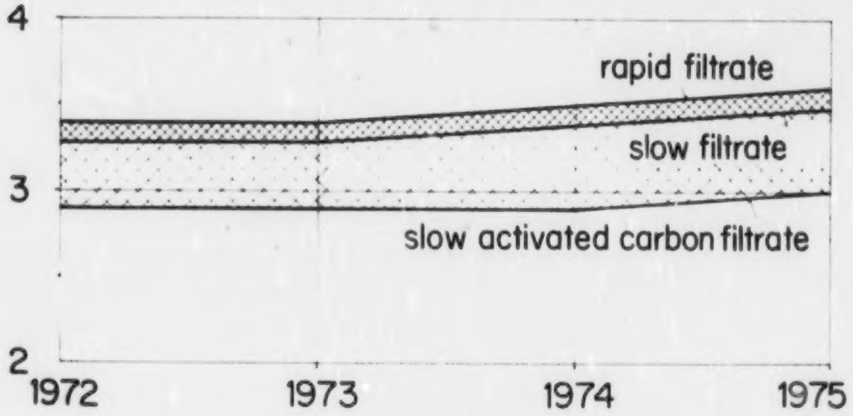


Fig.21 Moos lakewaterworks; COD in mg O_2/l in rapid and slow filtrate

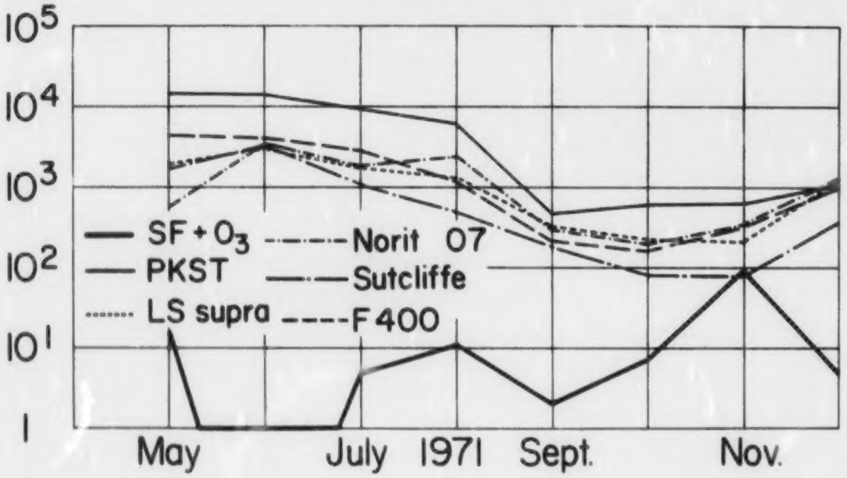


Fig.22 Test I; bacterial count after 3 days at 20° C in 1 ml of chlorinated rapid filtrate and various activated carbon filtrates (59 samples)

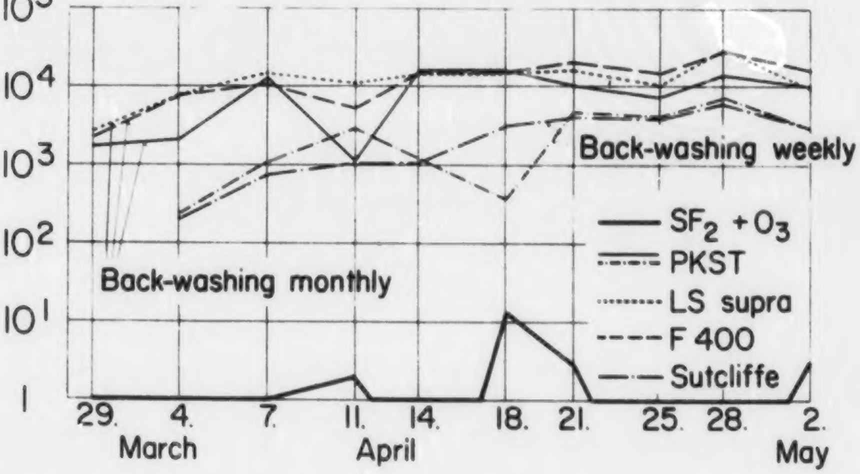


Fig.23 Test 2; bacterial count after 3 days at 20°C in 1 ml of ozonised slow filtrate and various activated carbon filtrates (10 samples)

after 5 weeks were shown to have a recurrent tendency for these carbon types, e.g. about 60% . Hence, it must be concluded that the carbons have a significantly lower tendency towards reinfection upon backwashing the AC filter more often. Full-scale tests with rapid filters of the works "Lengg", charged with AC, confirmed this assertion. In past experiments the AC Lurgi LS-Supra and Norit PKST did not lead at all to reinfection; however, they were fed with chlorinated water. The new AC-filter in "Lengg" -they are backwashing twice a week- never exhibited a value of more than 10 to 50 germs per cubic centimeter. These are extraordinary results (Fig.24).

6. Reactivation

Fig.25 shows the reactivation-oven installed in the water works. The reactivation is done by the so-called "fluid-bed process" from Norit. It is assumed that the AC must be either replaced or reactivated every one or two years. The fluid-bed process was chosen because it shows the lowest loss of carbon of all processes available on the market. The efficiency of the reactivation can be seen in Fig.26. The author was present when Norit ROW 08 Supra from Duisburg and PKST 1-3 from the work Zurich were reactivated. Later, they reactivated another charge of soft carbon, Norit PKST 1-2, i.e., a light AC in the same oven. Although this carbon is not usually suitable for reactivation, the losses were only 50% in comparison with common processes. The effectiveness of the reactivation is excellent. The PKST-carbon had only a small load of 28 g/kg. Whereas fresh carbon had a load of 5 g/kg, the value for the reactivated carbon was slightly higher, namely, 8 g/kg (Fig.27). Such a reactivation plant is now installed in the lake water-works "Lengg" and was set in operation at the beginning of 1976, i.e. when the reactivation of

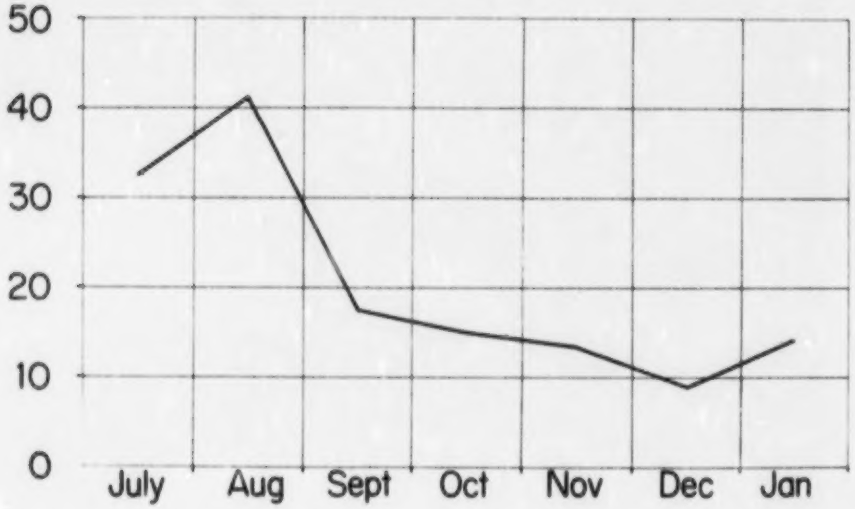


Fig.24 Lengg lakewaterworks; bacterial count after 3 days at 20°C in 1 ml of activated carbon filtrate of the "South" installation

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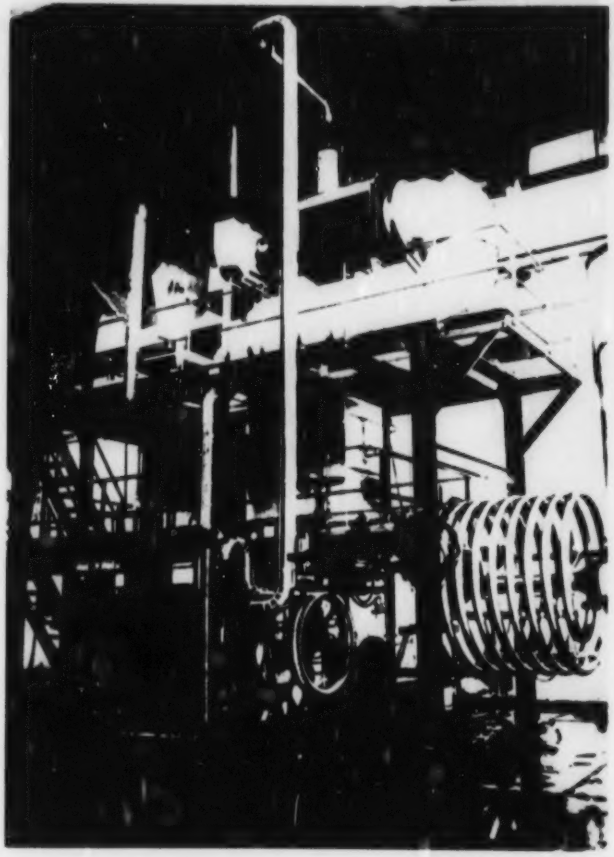


Fig.25 Norit reactivation furnace, fluidized-bed process

	DMF extract g/kg AC			DMF exract extinction at 300 nm d = 1 cm		
	total load	new	regenerated	total load	new	regenerated
Duisburg ROW 0,8 supra Water throughput per kg AC unknown	28,5	1,6	3,1	1,576	0,044	0,066
Zurich PKST 1-3 Water throughput per kg AC of 3800 m³	20,9	2,2	4,5	1,055	0,045	0,057

Fig.26 Reactivation efficiency of various activated carbon types, reactivated in the Norit installation on March 26th 1974

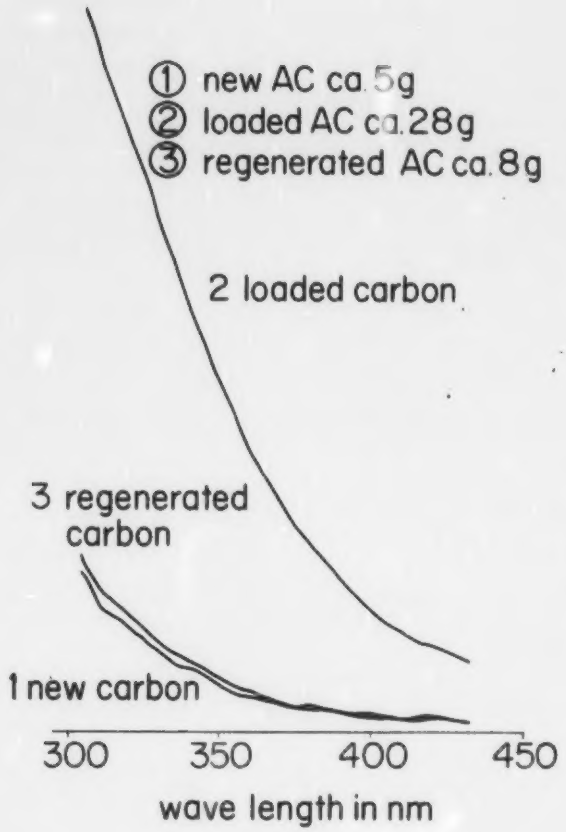


Fig.27 Results of the activated carbon reactivation; UV-spectra of the DMF-extracts

the used Pittsburg-400-carbon was necessary. Further results therefore can only be published later. The plant is usually operated with natural gas which is environmentally sound.

Construction of the AC filters in Zurich

In Lengg there are a total of twelve AC filters in use, specifically, six on each side of the pumping station. these are closed pressure filters of smooth-faced concrete with an area of 44 m^2 each (Fig.28). They have a bottom with 75 plastic nozzles per m^2. The filters are charged with a layer of quartz sand, 50 cm thick,- grain size 0.7-1 mm, and above with a layer of Pittsburgh F 400 AC of 1.2 m thickness. As this carbon shows a very high filtration resistance , it is replaced during the reactivation by the very good AC Norit ROW 08 supra. With the latter, there is a considerably smaller pressure loss. Nevertheless, the Pittsburgh carbon has very good characteristics and it is therefore still used in the lake waterworks Moos, where pressure losses cause no problem.
The cleaning of the AC filter is accomplished by backwashing with pure water, that is, with water of the same which is used for the rapid filters. The back-washing velocity is 25 m/h; if necessary it can be increased to 50 m/h. The back-washing can also be done with air. The normal velocity of the filter is 21.5 m/h if one of the twelve AC filters is backwashing. For reactivation the AC can be transported hydraulically to their respective reactivation plant silos. In the construction of the filters, measures must therefore be taken to ensure that enough free space is available for the swelling of the carbons, which is often greater than stated by the supplier (Fig.29). The construction of recharge basins as two-layer filters, e.g. with 10 cm AC, can be seen from Fig. 30.

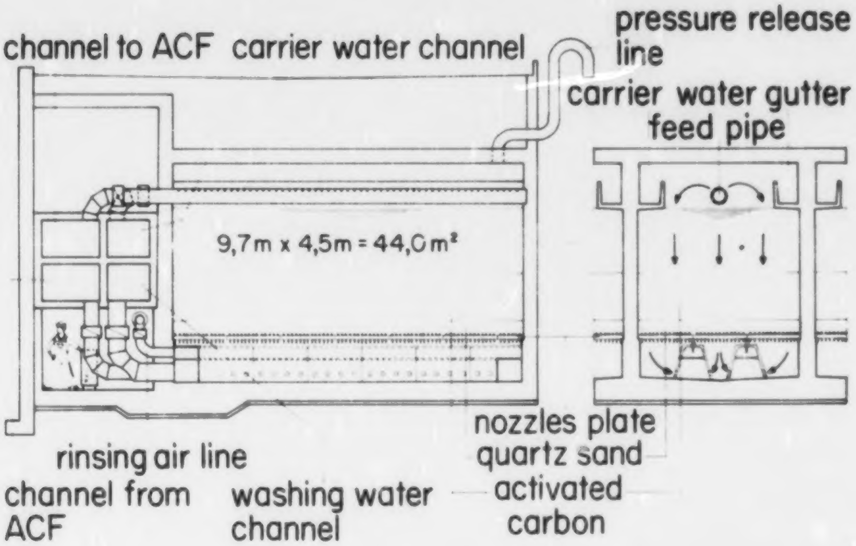

channel to ACF
carrier water channel
pressure release line
carrier water gutter
feed pipe
9,7m x 4,5m = 44,0m²
rinsing air line
channel from ACF
washing water channel
nozzles plate
quartz sand
activated carbon

Fig.28 Lengg lakewaterworks;Profile and cross-section of an activated carbon filter

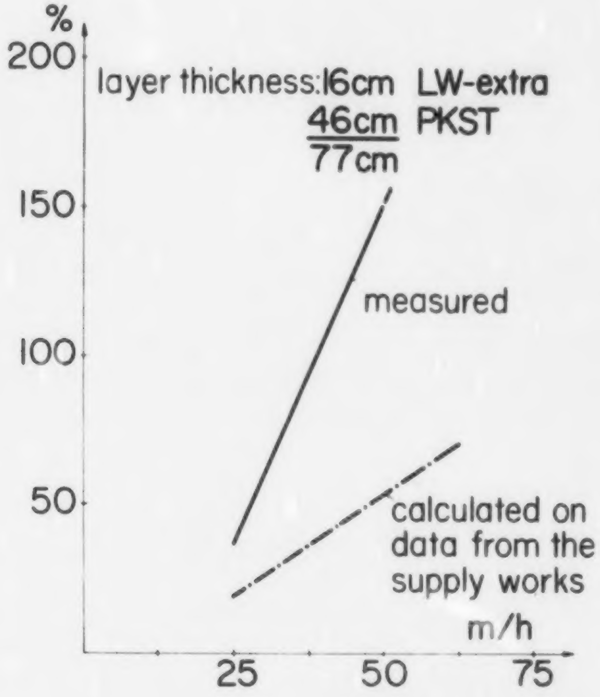


Fig.29 Multi-layer activated carbon filter; expansion of the activated carbon layers in % as a function of the flushing rate

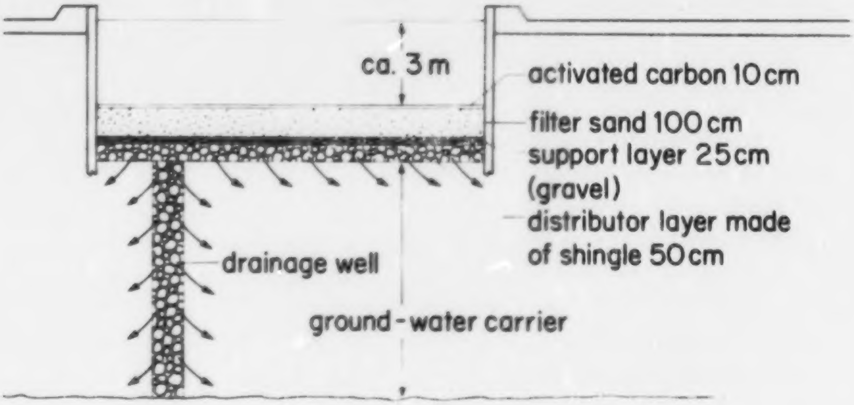

ca. 3 m
activated carbon 10 cm
filter sand 100 cm
support layer 25 cm
(gravel)
distributor layer made
of shingle 50 cm
drainage well
ground-water carrier

Fig.30 Composition of the enrichment basin at Hardhof; 10 cm of activated carbon are placed above the slow **sand filter**

8. The Costs of AC filtration

The construction costs for the 12 AC filters with a total area of 528 m^2 and a daily output of 250'000 m^3 are as follows:

Buildings	$	1'912'480	
Technical installations	$	2'260'520	*
Consolidation of the filter	$	90'280	
Total	$	4'263'280	

The costs of the reactivation plant are not included in this list. The capital costs per cubic meter daily capacity are therefore $ 17.--.The whole lake water treatment in "Lengg" including pumping station, will cost $ 170.-- daily/cubic meter, i.e., for the AC filtration 10% of the capital costs must be spent. The operating costs for interest and amortization (25 years,6% interest)are $ 400'000.-- each year. $ 80'000.-- should be included as annual maintenance costs. With an annual output of the works of 40 million m^3 the capital investment costs are therefore 0,01 $/$m^3$. The operating costs for the annual reactivation result in the following figures:

Construction costs of the reactivation plant and transfer installations ($ 400'000.--) (10% amortization, 6% interest)

capital costs	$ 80'000.--
maintenance	$ 20'000.--
heating	$ 16'000.--
service	$ 16'000.--
loss AC ca. 5%	$ 28'000.--
annual total operation costs	$ 160'000.--

With a water output of 40 million m^3 per year the operation costs for the reactivation including loss of AC are 0.004 $ per m^3. The total costs will be 0.016 $ per m^3 . With an annual output of 40 million m^3 the treatment

---

* including $ 640'000.-- for the AC

costs of the works at Lengg total $ 0.13 per m^3. Thus the costs for AC filtration come to only 12.5% of the total operating costs.

As the quality of the drinking water derived from surface water must not be inferior to that of perfect well - or ground water, the AC filtration is indispensable. The expenses for it are 1/8 of the total treatment costs, so the use of AC is also economically feasible.

Summary

ACs are principally available in Switzerland for the removal of organic substances as well as for the removal of oxidizing agents, such as chlorine.

The dechlorination efficiency of most ACs is good; however, it is decreased with time, so the ACs must be reactivated or replaced for this reason. The finer the grain size of the ACs, the higher the dechlorination efficiency.

ACs can be used very well as a second layer for the rapid and the slow filtration systems. As a result, the duration of the operating time is increased by at least five times keeping the same cleaning efficiency. The load of AC with organic substances can reach a level of about 80 g/kg (DMF-extract). Even with this charge, the reduction of the parameters, as determined by DOC and UV, remains good over a longer period, this for the ACs of the rapid filters as well as for the slow filters. The DMF-extraction-capacity is therefore not necessarily a criterion for changing the ACs.

AC can lead to reinfection, too. This is, among other reasons, a result of poor backwashing or of intervals between backwashing, which are too long. By backwashing the ACs twice a week, the number of bacteria in the lake waterworks at Lengg did not exceed 50/cm^3. Suitable ACs such as Pittsburgh 400, Lurgi LS Supra and Norit ROW 08 are well suited for reactivation.

It must be considered for the construction of the AC filters that enough free space is provided, as the swelling of the Ac during the backwashing is sometimes higher than reported by the supplier.

The total operating costs of the AC filtration are $ 0.016 per meter cube in Zurich; this corresponds to 12.5 % of the total operating costs of the lake water-works Lengg. As treated surface water must not be inferior to unobjectionable well- or ground water, an AC filtration system is necessary. Economically, it is feasible.

EXPERIENCES WITH PILOT PLANT ACTIVATED CARBON FILTERS IN DUTCH WATERWORKS

by W.C. van Lier (Amersfoort), A. Graveland (Amsterdam)
J.J. Rook (Rotterdam) and L.J. Schultink (Bloemendaal)

In the near future several Dutch waterworks will use granular activated carbon for water treatment. During the past few years these waterworks have been carrying out experiments in pilot plants. The results reported here were obtained at

Amsterdam-Leiduin (Municipal Waterworks)
Andijk (Provincial Waterworks of North-Holland)
Rotterdam (Waterworks)

all of which have quite different raw waters. In Fig. 1 the treatment steps which the raw (surface) waters were subjected to prior to the carbon treatment are shown.

In the Rotterdam and Andijk pilot plants an analysis of the activated carbon system itself was carried out. The influence of (apparent) linear velocity, height of the carbon layer and (apparent) contact time on the service time of the carbon (i.e. the time between two consecutive reactivations) were examined. The range of the variables investigated are shown in Tables I and II.

In Amsterdam three different treatment sequences were investigated parallel to each other. The (apparent) linear velocity was 8 $m^3.m^2.hr^{-1}$, height of the carbon layer 2 m.

Whereas in Andijk and Rotterdam the pilot plants were supplied with drinking water (i.e. finished-water quality), the carbon in the Amsterdam pilot plants formed part of a whole treatment sequence. The water quality is expressed in parameters as UV-absorption (λ = 240 nm, l = 4 cm, nitrate correction), DOC (dissolved organic carbon), $KMnO_4$ consumption, colour and taste. Determination of the DOCl (dissolved organic chlorine),

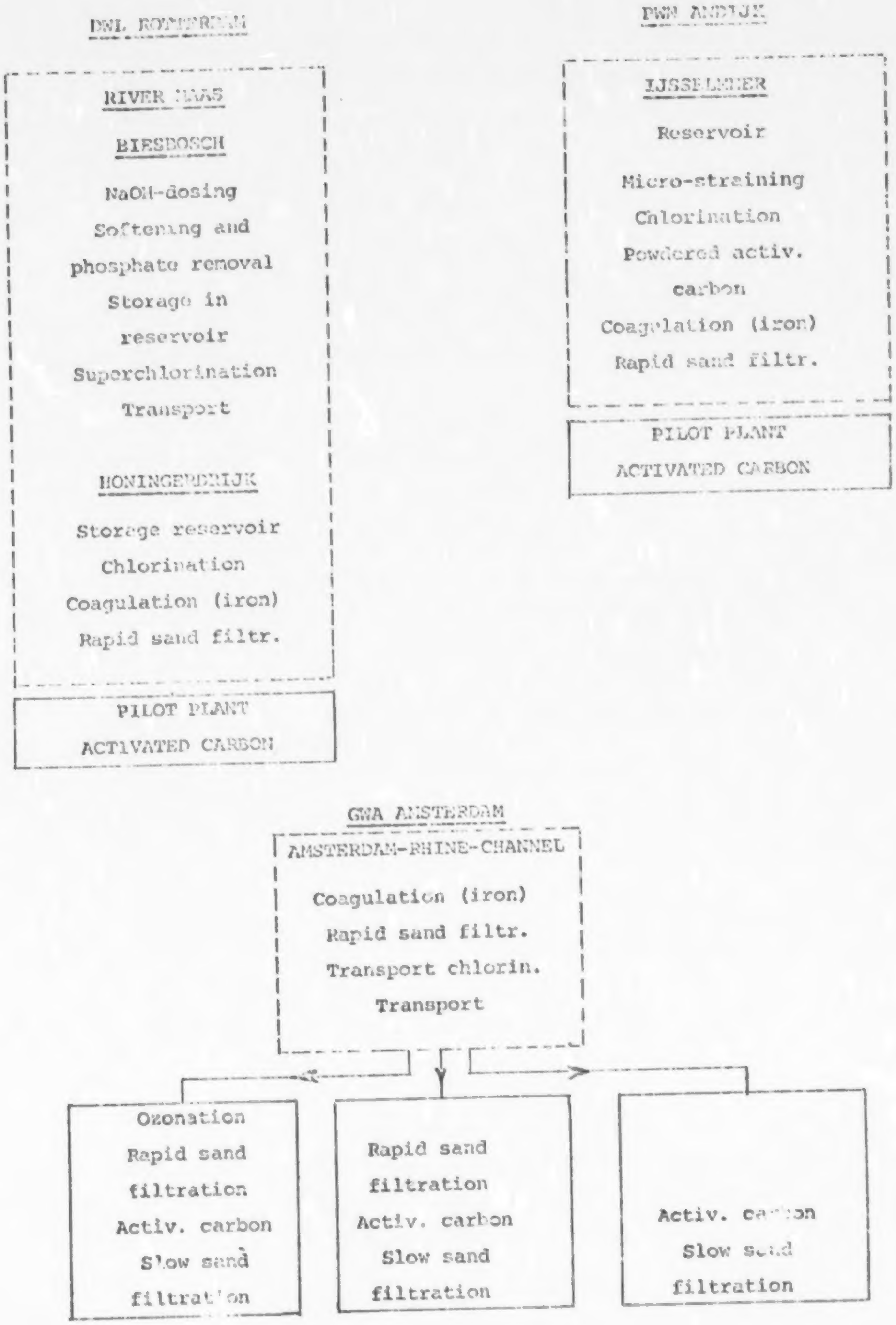

DWL ROTTERDAM
RIVER MAAS
BIESBOSCH
NaOH-dosing
Softening and
phosphate removal
Storage in
reservoir
Superchlorination
Transport
HONINGERDIJK
Storage reservoir
Chlorination
Coagulation (iron)
Rapid sand filtr.
PILOT PLANT
ACTIVATED CARBON
PWN ANDIJK
IJSSELMEER
Reservoir
Micro-straining
Chlorination
Powdered activ.
carbon
Coagulation (iron)
Rapid sand filtr.
PILOT PLANT
ACTIVATED CARBON
GWA AMSTERDAM
AMSTERDAM-RHINE-CHANNEL
Coagulation (iron)
Rapid sand filtr.
Transport chlorin.
Transport
Ozonation
Rapid sand
filtration
Activ. carbon
Slow sand
filtration
Rapid sand
filtration
Activ. carbon
Slow sand
filtration
Activ. carbon
Slow sand
filtration

Fig. 1 : Treatment of the water supplied to the activated carbon filters.

h (m)	0.5	1.0	1.5	2.0	2.5	3.0
v ($m^3.m^{-2}.hr^{-1}$)						
7.5	4	8	12	16	20	24
15.0	2	4	6	8	10	12
30.0	1	2	3	4	5	6

Table I : Pilot plant Rotterdam. Values of the (apparent) contact time (min.) as a function of height of the carbon layer (m) and the (apparent) linear velocity (v).

τ (min.)	h (m)	v ($m^3.m^{-2}.hr^{-1}$)
7.5	1.25	10
7.5	2.5	20
15	1.25	5
15	2.5	10
22.5	3.75	10
30	1.25	2.5
30	2	4
30	5	10

Table II : Pilot plant Andijk. Values of (apparent) contact time (τ), height of the carbon layer (h) and (apparent) linear velocity (v).

according to the method developed by SONTHEIMER and coworkers, was made on several occasions. However, due to the limited number of measurements they are not reported here.

All the experiments described here were performed with the same carbon, ROW 0.8 Supra, a NORIT product.

Results obtained at Amsterdam

The results obtained at the three pilot plant installations in Amsterdam are given in Fig. 2. This Figure shows the quarterly averages of a number of quality parameters after each treatment step. In addition to these, the average values over the whole testing period are given for turbidity, taste and the frequency of cleaning of the slow sand-filters.

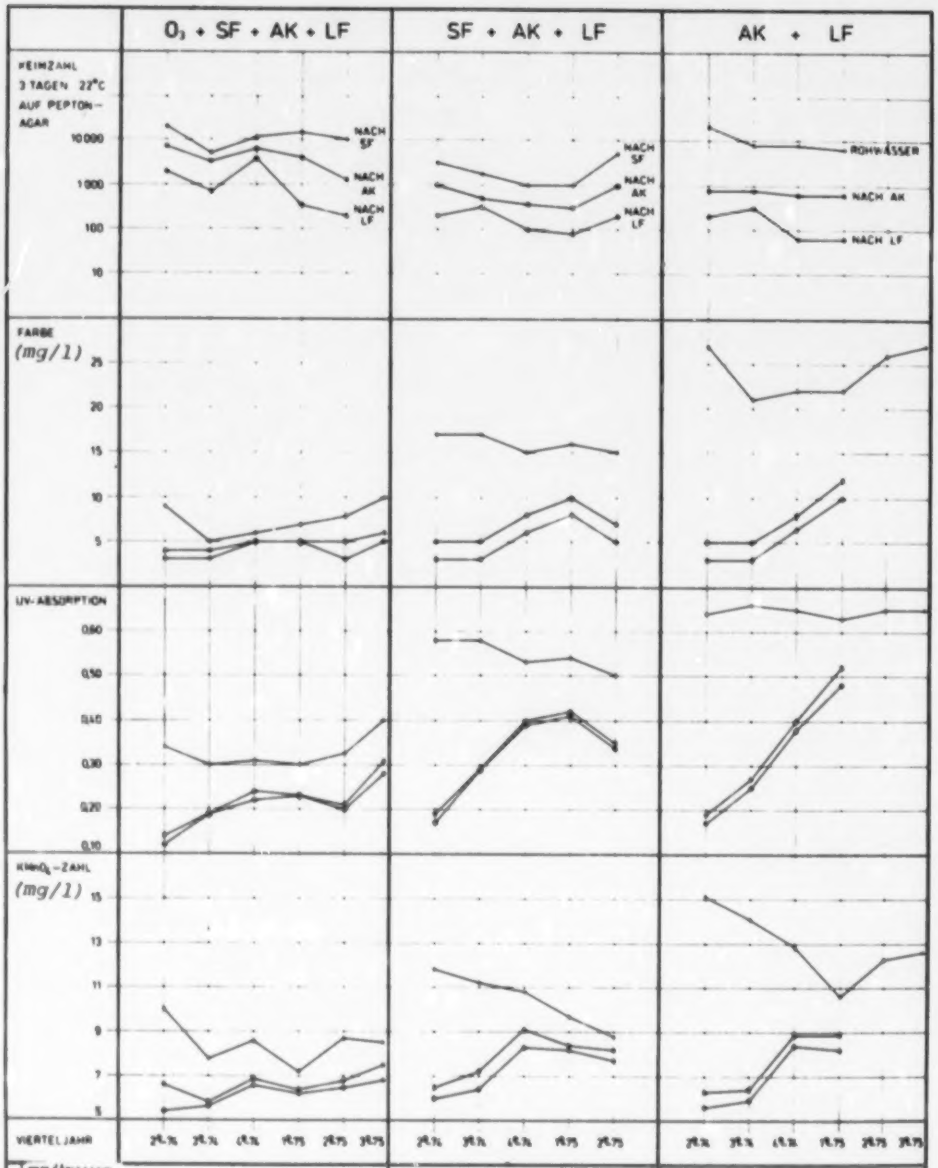
The following conclusions may be drawn:

1. Ozonation considerably increases bacterial count after rapid and slow sand filtration.

2. With regard to colour, UV absorption and $KMnO_4$ consumption, the final quality of the first system (ozonation etc.) is better than that of the two systems without ozonation.

3. Whereas the final water quality for the two systems without ozonation does not show a great difference, there exists a very important difference between the cleaning frequency of the slow sand filters. In this particular case, the replacement of the sand in the rapid filters by activated carbon does not seem to be attractive.

4. Slow sand filtration reduces bacterial count, colour and $KMnO_4$ consumption in all three systems.



LANGSAMFILTER	O₃ + SF + AK + LF	SF + AK + LF	AK + LF
TRÜBUNG (J.T.U.)	0,37	0,39	0,35
GESCHMACKSZAHL	0,2	0,2	0,2
REINIGUNGSFREQUENZ DER LANGSAMFILTER	3	5	16

O₃ = Ozonierung, SF = Schnellfiltration, AK = Aktivkohlefiltration, LF = Langsamfiltration

Figure 2. - Results in Amsterdam

Keimzahl: countings
3 Tagen 22°C: 3 days 22°C
auf Peptonagar: on peptone-agar
nach: after
Rohwasser: raw water
Farbe: color
$KMnO_4$-Zahl: $KMnO_4$ number
Vierteljahr: 3 month
Trübung: turbidity

Geschmackszahl: taste number
Reinigungsfrequenz der Langsamfilter: purification frequency of slow filters
nach Langsamfiltr: after slow filtration
O_3: Ozonation
SF: rapid filtration
AK: activated carbon filtration
LF: slow filtration

In Fig. 3 the results obtained at Amsterdam on the influence of the final water quality after slow sand filtration on the service time of the activated carbon are shown. The service time is defined as the period during which the value of a quality parameter (in this case the UV absorption) in the final effluent does not exceed a pre-determined value. The values of the service time have been calculated as follows. The "breakthrough curves" are described by one of the three following purely empirical equations:

$$\text{Log } (\Delta\%) = A_1 \log T + B_1$$

$$\text{Log } (\Delta\%) = A_2 T + B_2$$

$$\text{Log } c = A_3 \log T + B_3$$

where:

$\Delta\%$ = percent reduction of the UV absorption over the whole pilot plant at time T

c = value of the UV absorption after slow sand filtration at time T

In each case that equation was used which gave the highest value of the correlation coefficient, the values of which ranged from 0.8 to 0.9.

It may be seen that the difference in service time between the two systems without ozonation is insignificant, whereas the service time for the system with ozonation is much longer.

Application of the same method to the values of the $KMnO_4$ consumption leads basically to the same results. Unfortunately the DOC values were not measured in Amsterdam. One should realise that the effect of ozonation on the DOC value is generally much lower than the influence on UV absorption and $KMnO_4$ consumption.

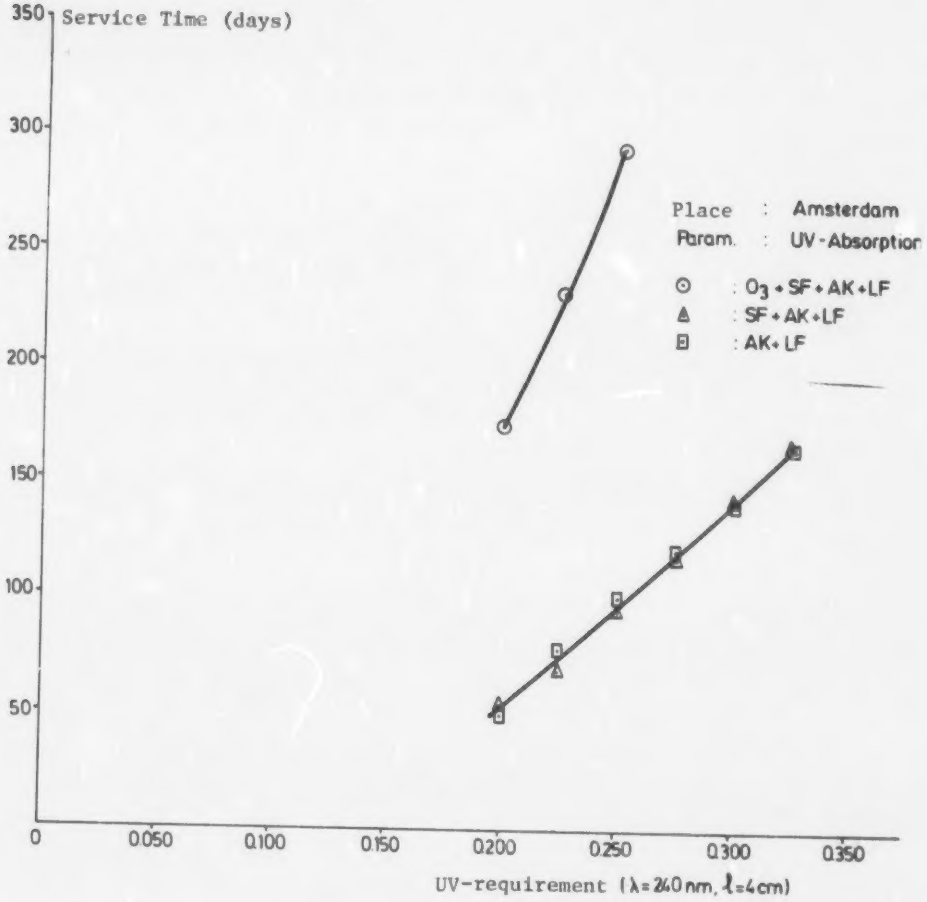


Figure 3: Service time as a function of the filtrate quality

Results obtained at Andijk and Rotterdam

In the main, discussion is restricted to the results obtained with the DOC as quality parameter. A rather unconventional method to process the measured DOC values was chosen in order to evaluate the water quality after the activated carbon filtration. From the DOC values, measured once or twice a week in influent and effluent of a filter, the total quantity of DOC applied to the filter (expressed e.g. as kg DOC per m^2 of filter area) was calculated together with the total quantities of DOC removed by the carbon (e.g. kg DOC per m^3 of carbon), and the DOC in the effluent of the filter as a function of time. From these quantities over any period of time it was possible to calculate the average DOC value before or after the carbon over the same period. All requirements regarding the quality of the effluent are either expressed as cumulative quantities (e.g. kg DOC applied per m^2 of filter area) or as an average value in the total quantity of water before and after filtration (e.g. gram DOC per m^3 of water).

We shall deal with the following three aspects of activated carbon filtration as a treatment process.

(a) Influence of the (apparent) linear velocity at constant contact time

(b) Influence of the season (i.e. the water temperature)

(c) Influence of the (apparent) contact time and water quality requirements at constant linear velocity

Table III shows the effect of the linear velocity at constant contact time. This Table gives the value of the service time as a function of the quality target and linear velocity for a number of contact times. For a given value of the contact time (e.g. 4 minutes) we have calculated from the experimental DOC values how long the service time is for three values of the linear velocity in the treatment of a constant volume of water per hour (identical in all three cases) and using the same quantity of carbon.

Target		$\ddot{c}$ (gr.m^{-3}) $\bar{\bar{\delta}}$ % Reduction	3.80 10	3.38 20	2.96 30
τ (min)	h (m)	v (m^3.m^{-2}.hr^{-1})			
4	0.5	7.5	152	28	
4	1.0	15	150	37	
4	2.0	30	141	28	
6	1.5	15	197	52	
6	3.0	30	172	73	
8	1.0	7.5	270	90	
8	2.0	15	240	61	
12	1.5	7.5		144	49
12	3.0	15		137	52

Table III : Effect of linear velocity (v) at constant contact time (τ). Value of the service time (days) in relation to target and velocity.

The faults, inherent in the method, may be a possible explanation for the discrepancies between the various results because, with the possible exception of the results for t = 8 minutes, no systematic influence of the linear velocity on the value of the service time was obtained. In any case, it can be seen that the effect of contact time and quality requirement on the service time is much greater.

Application of the same method to the UV absorption and the $KMnO_4$ consumption confirmed the results described above. In conclusion it may be said that at constant contact time the effect of the linear velocity on the service time is comparatively small, at least when dealing with quality parameters such as UV absorption, DOC and $KMnO_4$ consumption.

The effect of the seasonal variation in the water is shown in Fig. 4, where the amount of DOC, taken up by the carbon (expressed as kg DOC per m^3 of carbon) is related to the amount of DOC applied to the carbon (kg DOC per m^2 of filter area). With the same amount of DOC applied the amount taken up by the carbon during the summer is considerably higher than the amount taken up during the winter run. This difference can be explained by the action of biological processes in the carbon filters. These biological processes manifest themselves in the oxygen consumption by the carbon filters. In winter this consumption amounts to approx. 6×10^{-3} g O_2 per kg of carbon per hour, while in the summer it ranges from 24×10^{-3} to 30×10^{-3} gr O_2 per kg of carbon per hour (measurements at PWN, Andijk, t = 30 min.).

The influence of the contact time at constant linear velocity is shown in Fig. 5 and Table IV. Two marked effects are noticeable:

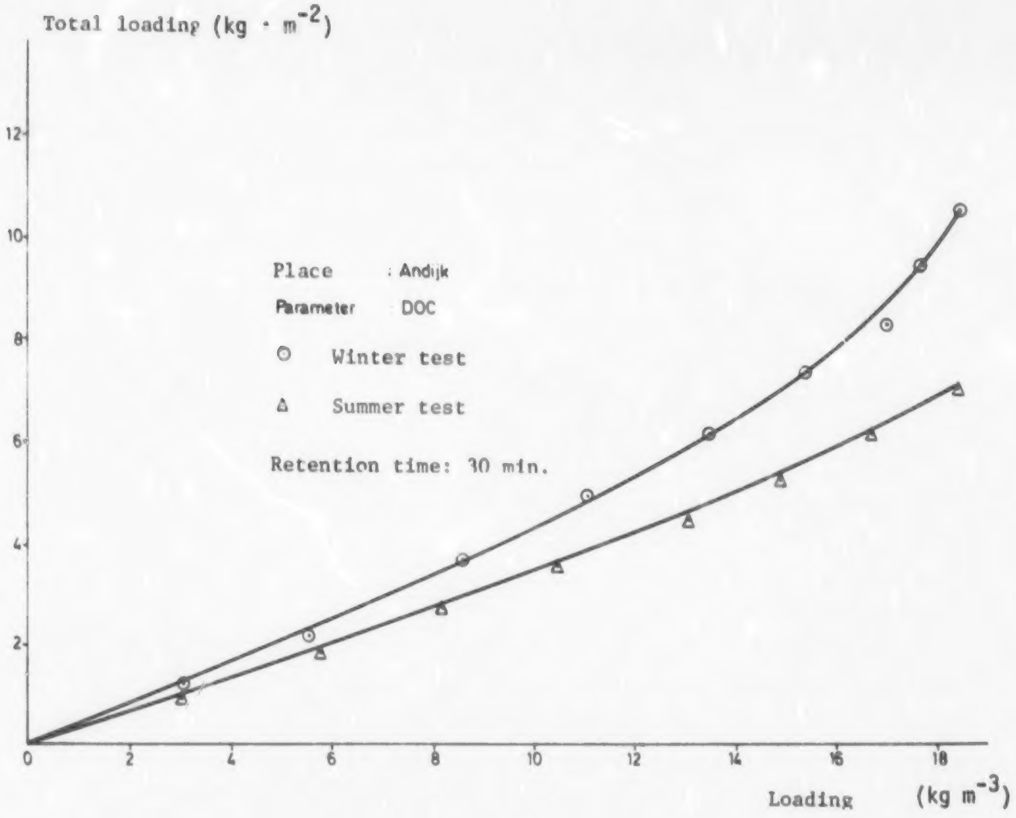


Figure 4: The effect of the seasonal loading (kg DOC/m^3) activated carbon) in dependence of the total loading

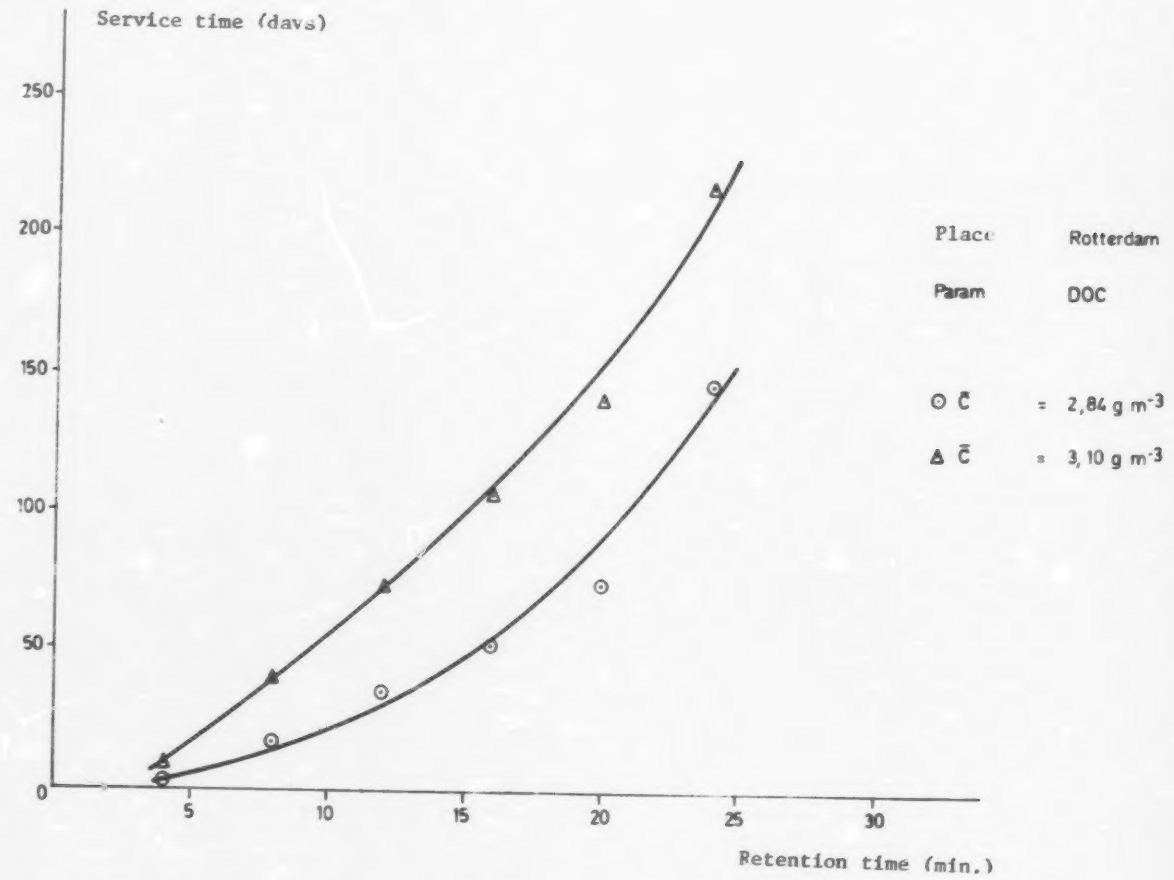


Figure 5: Service time as a function of the retention time.

Location	ROTTERDAM							ANDIJK	
Target $\bar{c}$ (gr.m^{-3})	2.84	2.90	2.96	3.01	3.06	3.11		2.05	2.11
Contact time (min.)							Contact time (min.)		
4	3	4	5	6	8	9	7.5	6	7
8	17	21	26	30	35	40	15	36	39
12	35	42	49	58	65	73	22.5	85	92
16	52	63	73	84	96	107	30	145	161
20	74	87	100	114	127	141			
24	146	156	172	188	203	218			

Table IV : Effect of **target** and contact time on service time (days).

1) a strong effect of contact time on service time;

2) a strong effect of the target on service time (an effect which is more marked for shorter contact times).

The UV measurements have been processed in an analogous way and give similar results, as is illustrated in Fig. 6. The service time is plotted as a function of the UV absorption target in the effluent averaged over the service time for Amsterdam, Andijk and Rotterdam. All curves relate to a contact time of 15 minutes. In Amsterdam we have chosen the results of the system: rapid sand filtration, activated carbon and slow sand filtration. While the average values for the UV absorption in the influent of the carbon filters in Andijk and Rotterdam do not differ greatly from each other, the UV absorption in the installation in Rotterdam is much lower. As we see, the quality of the raw water exerts a strong influence on the performance of the carbon.

When a waterworks starts using activated carbon and, for example, uses several filters in parallel, it may be advantageous to bring these filters into operation at regular intervals of time instead of putting them all into operation at the same day. This "time-spaced" operation has two advantages, the first of which is rather obvious. Where the exhausted activated carbon is (thermally) reactivated by the waterworks itself, much smaller reactivation facilities are required.

The second advantage can be a much longer service time of the individual filter contents as long as the requirements to the water quality permit a partial "breakthrough of a quality parameter". We shall prove this latter point on the basis of the results obtained for the DOC in the Rotterdam pilot plant.

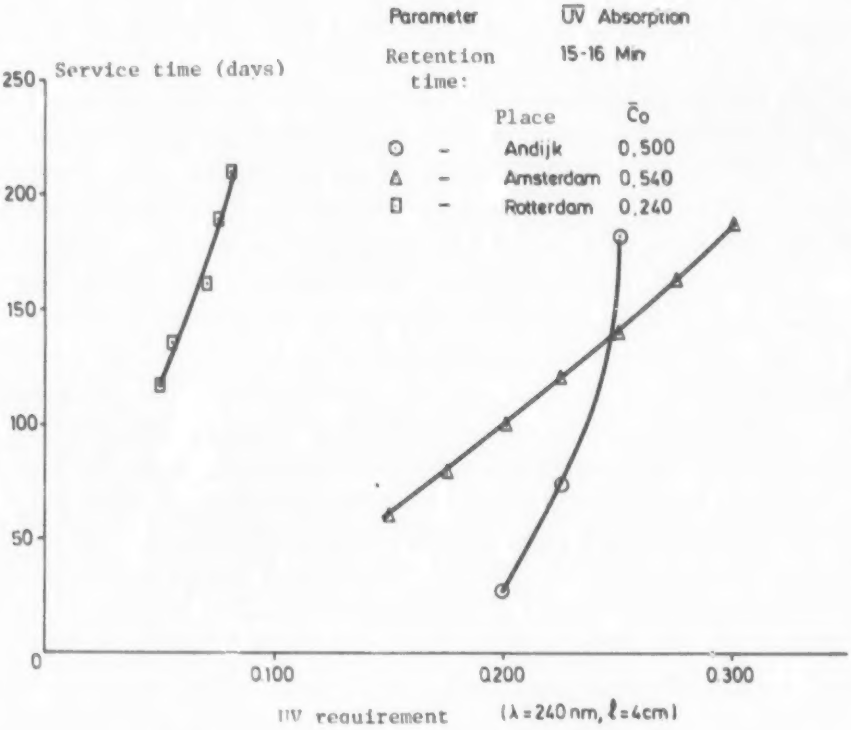


Figure 6: Service time as a function of the water quality requirement

Table V shows the values of the service time for two extreme cases:

(a) all filters are started simultaneously;

(b) the filters are put into operation at exact time intervals (e.g. 12 filters in parallel, service time for each filter one year, reactivation of the contents of one filter each month).

Let us assume that n be the number of filters, $\bar{c}$ the average DOC value in the effluent of one filter, $\bar{\delta}$ the average (percent) DOC reduction over a filter, where $\bar{c}$ is the average value over the service time. The average DOC value in the total effluent of all filters is $\bar{C}$, the average DOC reduction over all filters together is $\bar{\Delta}$. When the average DOC value in the final effluent must not exceed the value of 2.54 $gr.m^{-3}$ (i.e. an overall average DOC reduction of 40 %), the service time for the first basic case (simultaneous start) equals 37 days. When the filters are not simultaneously put into operation and the contents of a filter are reactivated (or replaced) as soon as $\bar{c}$ > 2,54 $gr\ m^{-3}$ (effluent of this filter), the service time T_L will become 82 days because the average overall value $\bar{c}$ = 2,15 $gr\ m^{-3}$ (for n = 18). When $\bar{C}$ must not exceed a value of 2.50 $gr.\ m^{-3}$ (n = 18), T_L even becomes 182 days if we use example 2. As one can see, the service time in the two above mentioned basic cases is completely different. A stepped start of the filters is for that reason essentially cheaper than a simultaneous start. The calculations above apply only for cases where a breakthrough > 0 in the overall effluent is permitted. If the water contains substances which must be completely removed, these calculations do not apply. In that case, however, a stepped starting is desired because of the size of the reactivation installation. This effect is presumably quite general because it is connected with the limited speed of the mass transfer processes and with the fact that only part of the organic matter contributing to parameters such as DOC, UV absorption etc. is adsorbed by the activated carbon. When carbon is used

$\bar{c}$ (gr. m^{-3})	2.96		2.54	
$\bar{\delta}$ % **Reduction**	30		40	
n	$\bar{\Delta}$	$\bar{c}$	$\bar{\Delta}$	$\bar{c}$
12	40.2	2.53	48.8	2.16
18	40.8	2.50	49.2	2.15
24	41.0	2.49	49.4	2.14
T_L (days)	172		82	
t_L (days)	82		37	

Table V : Effect of different starting times for the various filters on the average values of the water quality of the overall effluent and on the service time.

Parameter : DOC

Location : Rotterdam

for the decolourisation of sugar or glucose this effect is generally made use of.

Costs of carbon application

The results obtained in Rotterdam and Andijk have been used for an estimation of the costs of the carbon treatment. The basis of this calculation is shown in Table VI. It has been assumed that at constant contact time the effect of linear velocity on service time is smaller than 10 %, an assumption which, as one has already seen, is presumably correct.

Fig. 7 shows the results for Andijk, where the costs (expressed in cents (Dutch) per m^3 of treated water) are plotted as a function of contact time. We may draw the following conclusions.

(a) the contact time exerts a strong influence;

(b) with the exception of short contact times the costs with concrete filters are lower than those for steel filters;

(c) the optimum value of the contact time for concrete is lower than for steel filters.

These results were obtained on the basis of stringent requirements on the water quality (55 % reduction of DOC).

Fig. 8 gives some idea of the effect of the water quality requirements on the treatment costs. As one would expect, the requirements exert a strong influence on the treatment costs. The optimal value of the contact time depends on water quality requirements.

Two basic cases : Concrete Filters
Steel Filters
Water throughput : 6000 m3 per hour
Reactivation of the carbon : thermal, in the water works
Reactivation losses : 8% by volume
Depreciation : annuity
Interest : 9%

	Concrete	Steel
Number of filters	12	12-21
Diameter (m)		3.5-6.0
Height of carbon layer (m)	1.7-5.0	3.5-5.0
Linear velocity (apparent, $m^3.m^{-2}.hr^{-1}$)	10-20	10-52
Filter area (m^2)	20-50	

	Depreciation (years)	Maintenance (%)
Concrete	30	3
Steel	15	5
Control equipment etc.	10	6

Table VI : Basis of cost estimation.

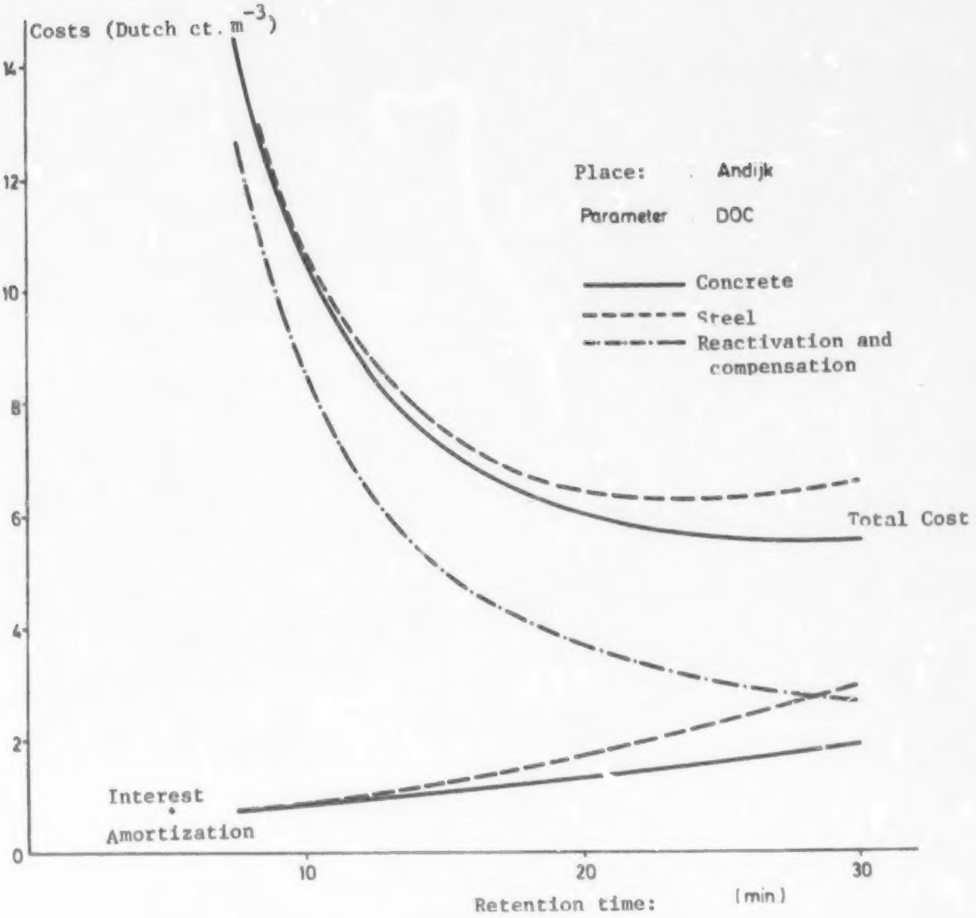


Figure 7: Costs of activated carbon filtration as a function of retention time.

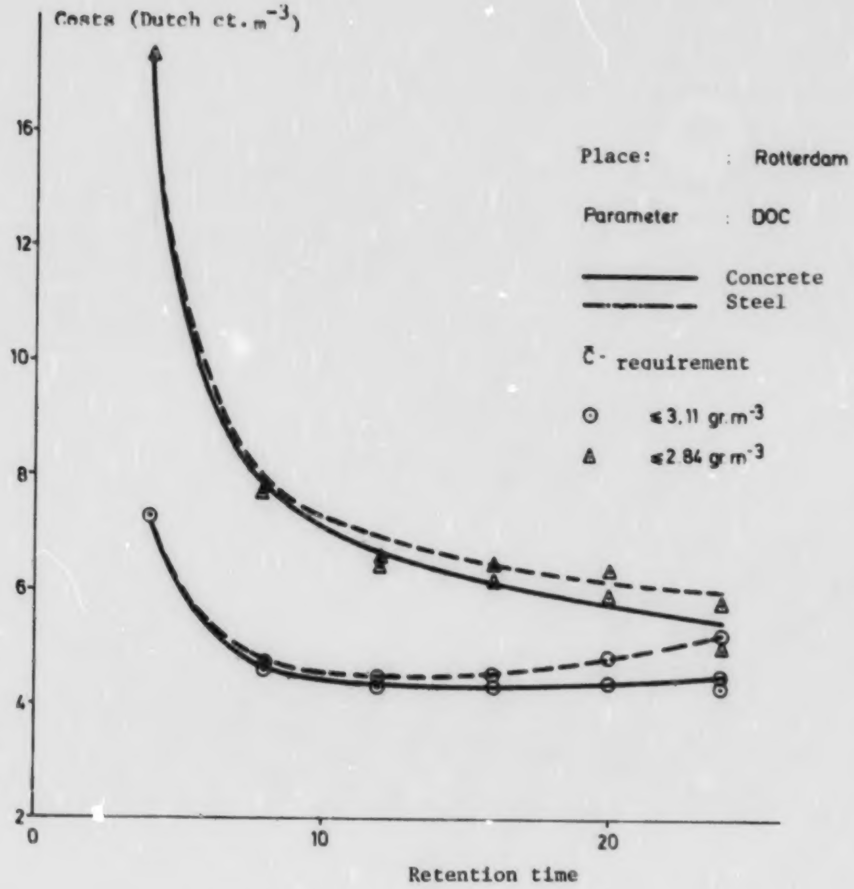


Figure 8: Total costs of activated carbon filtration as a function of the retention time.

Finally, one should realize that these two cost exercises must be regarded as illustrative to a possible method of operation. The starting points for this calculation (depreciation rate, reactivation costs etc.) play an important part, and it is possible to choose a completely different set of conditions. One may, however, state that when imposing rather strict targets regarding the water quality, a comparatively long contact time may be quite attractive from an economical point of view.

THE USE OF ACTIVATED CARBON TO ANALYSE NATURAL WATERS WITH REGARD TO THEIR BEHAVIOUR IN WATERWORKS FILTERS

by F. Fuchs and W. Kühn, Karlsruhe

The use of activated carbon as an analytical technique for the concentration of water-soluble organic substances was first described by BRAUS, MIDDLETON and WALTON (1951) and by MIDDLETON et al (1952). The extraction of the loaded carbon was carried out with ether and the extract was then broken up into 5 different fractions, in acid and alkaline media. Identification of the organic material was made using paper chromatographic techniques.

HOLLUTA took into consideration these studies when he investigated the river Rhine in 1953, at the Department of Water Chemistry of the University of Karlsruhe. In this case extraction of the carbon was carried out in several stages, using ether, pentane, benzene, and later on with chloroform (HOLLUTA, 1960). The carbon was loaded by shaking 40 l of water for 30 minutes with 20 g of powdered carbon. In 1962, it was possible to obtain about 2 mg of extract per litre, extracting the carbon with ether (HOLLUTA, 1959,1960). In comparison, today the control filter technique described in this paper produces about 8 mg/l, using di-methyl formamide as the extraction solvent. This quality, four times as great as in 1962, measured at the same river flow-rate. is not only due to the increased pollution of the Rhine, but especially to the higher loading obtainable on modern activated carbons, and a nearly quantitative desorption by DMF. Analysis of the extract reveals a polar, biodegradable fraction and a non-polar fraction, which constitutes about 20 percent of the total (HOLLUTA, 1964). Similar fractions of polar and non-polar material are found today. However, whereas formerly the most important of the non-polar compounds were mineral oil hydrocarbons, today analysis shows that the extensive group of lipophilic, frequently toxic, organo-chloro compounds are much more important.

HOLLUTA et al (1964) separated the non-polar compounds from the total extract chromatographically using Al_2O_3 followed by a subsequent elution with pentane. This method is still employed today in an improved form for this purpose. An elemental analysis of an activated carbon extract from the Lower Rhine gave values of sulphur between 3 and 5 per cent (HOLLUTA, 1964); these values also correspond to those obtained today.

In the USA extraction of the organic material adsorbed onto the activated carbon is carried out using chloroform and ethyl alcohol as solvents. This is the so-called CCE- and CAE-method (BUELOW, CARSWELL and SYMONS, 1973; STEVENS, 1974). The organic compounds, which are adsorbed onto the activated carbon, grain diameter 0.4 - 1.4 mm, are extracted in 2 stages with the above solvents. The conditions of adsorption as well as the extraction and evaporation procedure are exactly defined. The amount of extract found is determined gravimetrically. The limits proposed for drinking water are 0.7 mg/l and 3.0 mg/l for the chloroform and ethanol extracts, respectively. However, we have found the above procedure has some disadvantages. As a result of the low contact time only a relatively small part of the organic substances are adsorbed (see Table 1).

Table 1: Comparison of the CCE/CAE method with the DIOX/DMF method

	Filter Data				Extract obtained using same tpye of activated carbon
	activ. carbon g	Ds m^3/kg	FG m/h	VZ min	amount of extract g/kg activ.carb.
CCE/CAE	70	0.86	0.6	4.5	CCE/CAE: 14.2/16.3
DIOX/DMF	100	3.10	0.8	17	DIOX/DMF: 24.9/50.4

Ds = water throughput of filter
FG = filter velocity
VZ = retention time referring to void volume

In addition, chloroform is not miscible with water, so that the carbon must be pre-dried. It has the additional disadvantage that determination of chlorine in the extracted organic substances is no longer possible. Furthermore, the ethanol extraction is incomplete when compared with DMF. These problems led us to develop the analytical technique outlined in this paper.

In 1971, in this Institute,MAIER undertook research on the desorption of loaded activated carbon, examining the possibility of chemical regeneration of activated carbon. His results suggested a possible technique for the analytical separation of compounds adsorbed onto the carbon. On the activated carbon employed in practice, a great variety of organic compounds are always adsorbed. In an analytical technique it is important to distinguish between non-polar and polar substances and to employ correspondingly selective solvents.

Most of the organic substances soluble in water coming from a natural origin have polar properties. For that reason, the first step in an extraction cannot be carried out using a polar solvent like DMF or DMSO. In this case the small quantity of non-polar compounds, such as the chlorinated hydrocarbons would be included in the extract of the polar substances, since the non-polar compounds are generally less than 10 percent of the total loading. For this reason, in the first stage the non-polar or substances of low polarity are separated with a non-polar solvent, and then subsequently the polar substances are extracted with a polar solvent. Some results obtained with different solvents are shown in Table. 2

There are few non-polar solvents which are water-soluble, of these dioxane proved to be satisfactory. This compound, on the one hand, is able to dissolve non-polar substances, while at the same time it is miscible in water at any ratio, because it is a symmetrical ether and therefore able to form hydrogen bonds.

Table 2: Extract yields from activated carbon, dipole moments and solubility in water of various solvents

Solvent	Extract yield g/kg act.carb.	Dipole moment Debeye	Solubility in water
Carbon Disulphide	0.4	0	-
n-hexane	0.5	0	-
Cyclohexane	1.0	0	-
Carbon tetrachloride	1.5	0	-
Benzene	2.1	0	-
Chloroform	2.5	1.05	+
Dioxane	4.4	0	+++
Ethanol	9.6	1.70	+++
Acetone	10.9	2.84	+++
Dimethylformamide	29.7	3.80	+++

The hydrogen-bonding property of dioxane is responsible for the removal of only small quantities of polar compounds. The great proportion of the polar material is then desorbed using DMF. In spite of the fact that the extraction of the compounds on the activated carbon is almost complete, it cannot be avoided that a great deal of the low boiling point, volatile, organic compounds are lost because the relatively high boiling point of dioxane (102 °C) and DMF (154 °C), necessitate the use of vacuum distillation for their complete removal. A great deal of effort has been expended to improve the analytical technique.

PARK (1974) found an improved method of eluting the carbon at normal temperature. Also, the low boiling substances may be measured by the Headspace-method or the stripping technique devised by GROB (1973,1974), which is an accumulation method on activated carbon. STIEGLITZ (1975) has successfully employed this method in his research of the river Rhine. The results, including only the main compounds, are shown in Table 3.

Table 3: The main components of easily volatile compounds in the river Rhine at Karlsruhe

Definition	Boiling point	Definition	Boiling point
Cyclohexane	80	Dichloro benzene	179
Trichloro ethylene	87	Isobutyl benzene	170
Toluol	110	Hexachloro ethane (subl.)	185
Tetrachloro ethylene	121	Tetrachloro butadiene	188
Monochloro benzene	132	Pentachloro butadiene	-
Xylol	142	Trichloro benzene	213
Tetrachloro ethane	147	Hexachloro butadiene	215
Bromo benzene	156	Dodecane	215
Cumene	163	Tetradecane	252
Mesitylene	159	Pentadecane	270
Isocumene	159		

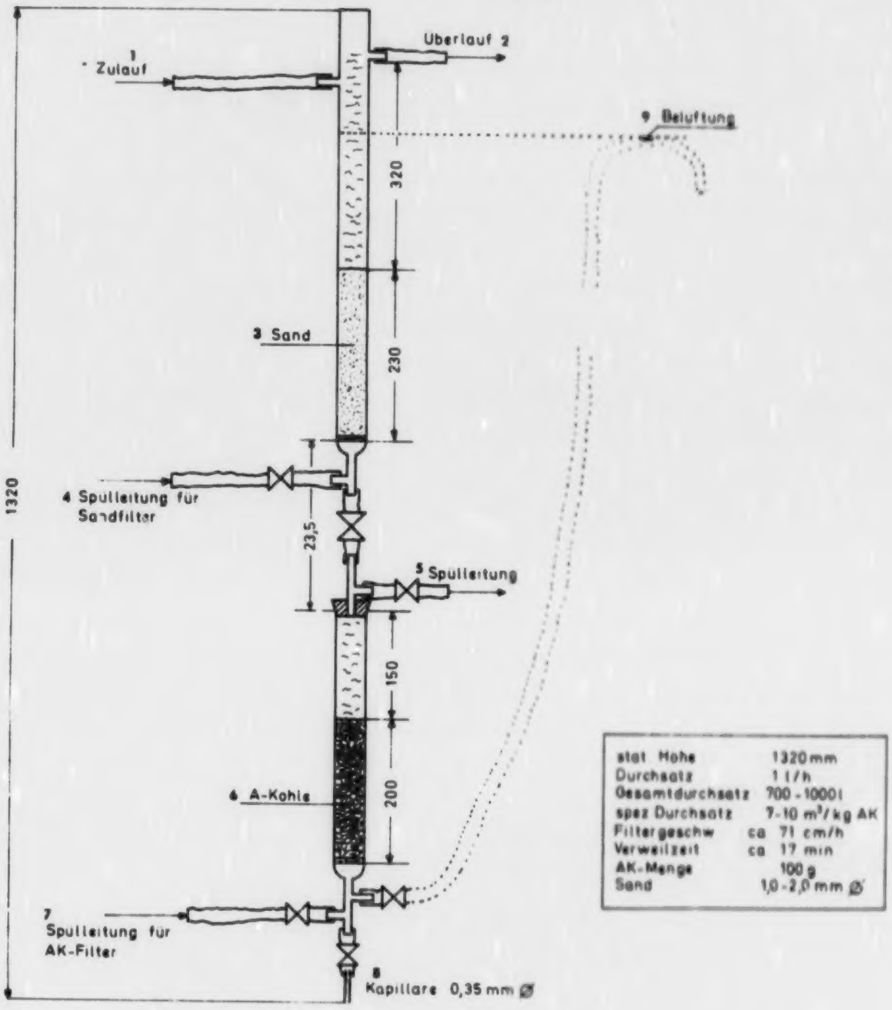
In this Table, the compounds are listed according to their retention time in a gas-chromatograph, which roughly corresponds to the increasing boiling point. At the same time about 100 compounds, which were all identifiable, where determined using the stripping method with the same surface water.

The analysis of organic substances in water, as practised in the Institute for the last two years, makes use of accumulation on activated carbon control filters. During this period about 50 control filters have been in operation, and a large quantity of data has been obtained.

The apparatus (Fig. 1) is simply constructed,so it can be operated in a waterworks without any trouble. The filtration velocity of 0.7 m/h is very low, therefore even in very polluted water an breakthru DOC value can be measured after a filtration quantity of 300-400 litres. If the water contains little organic material the filtration quantity for 100 g activated carbon may be 1000 litres or more before a break-through of the filter occurs. The loading of the carbon should be at least 1 - 2 per cent of the carbon weight, to ensure that the zero value is not more than 5 per cent of the loading.

Fig. 1

To guarantee good adsorption kinetics, a finely granulated activated carbon, for instance F 400 or finely granulated LSS, is used in the control filters. The sand filter, arranged above the activated carbon filter, removes colloid or suspended particles and gases if the water is supersaturated. In contrast to the analysis of individual samples, an average value measured over a longer time is obtained. Nevertheless, this method has also disadvantages as only about 60 per cent of the dissolved organic substances are found again in the concentrated extract, as can be seen in Table 4.


1 Zulauf
Überlauf 2
9 Belüftung
320
3 Sand
230
4 Spülleitung für Sandfilter
23,5
5 Spülleitung
150
6 A-Kohle
200
7 Spülleitung für AK-Filter
8 Kapillare 0,35 mm Ø
1320

stat Höhe	1320 mm
Durchsatz	1 l/h
Gesamtdurchsatz	700 - 1000 l
spez Durchsatz	7-10 m³/kg AK
Filtergeschw	ca 71 cm/h
Verweilzeit	ca 17 min
AK-Menge	100 g
Sand	1,0-2,0 mm Ø

Fig. 1: Layout of the control filter

1 Zulauf: inlet 9 Belüftung: ventilation
2 Überlauf: overflow
3 Sand: Sand
4 Spülleitung für Sandfilter: backwash for sandfilter
5 Spülleitung. backwash discharge
6 A-Kohle: activated carbon
7 Spülleitung für Ak-Filter: backwash for activated carbon filter
8 Kapillare: capillary tube
stat. Höhe: static head
Durchsatz: throughput
Gesamtdurchsatz: total throughput
Spez. Durchsatz: specific throughput
Filtergeschwindigkeit: filtration rate
Verweilzeit: contact time
AK-Menge: quantity of activated carbon

Table 4: Efficiency of control filters for measuring the dissolved organic substances

Sampling Station	organic subst. (from DOC) mg/l	adsorbed org.substances mg/l	non-polar org. substances mg/l
Lake of Constance	2.8	1.3	0.30
Rhine at Basel	5.6	2.9	0.36
Rhine at Duisburg	12.0	6.5	1.19
Neckar at Heilbronn	9.2	4.6	0.41
Fulda at Kassel	7.6	4.1	0.73
Ruhr at Mülheim	10.6	6.0	0.96
groundwater Karlsruhe	0.6	0.31	0.04
bank filtr. Düsseldorf-Benrath	5.0	4.4	0.87
bank filtr. Hamborn	6.0	5.3	0.66

This is due to the fact that substances such as carbohydrates are not readily adsorbed onto activated carbon. Furthermore, during an operation time of 6 to 8 weeks biological decomposition is also possible. Therefore the analysis of bankfiltrates leads to higher control filter efficiencies. This indicates that after ground filtration non-biodegradable compounds remain in the water. These compounds, important for the purification of water,are adsorbed by the control filter. In the mass balance, however, the low-boiling volatile compounds are absent, because they are lost at the distillation of the solvents.

Fig. 2: Schematic layout of analytical procedure

In Fig. 2 a schematic layout of the analytical procedure is shown. The activated carbon from the control filter is dried at 40 °C. One gram of it is used to determine the total chlorine of all organic compounds and the chlorides by pyrohydrolysis (KÜHN, SONTHEIMER, 1974). The inorganic chlorides are determined separately. To obtain the quantity of chlorine in the organic compounds, the amount of inorganic chloride must be subtracted from the pyrohydrolysis value.

A further quantity of 20 g dried activated carbon is extracted with dioxane and then with DMF. The liquid dioxane extract is immediately used to determine the amount of chlorine due to the non-polar chlorinated hydrocarbons, using a microcoulometer. Since it is possible to inject the dioxane extract directly into a gas-chromatograph, individual compounds may also be analysed. In this way the group analysis of non-polar chlorine compounds can be complemented by the identification of single chemical compounds. To find out the amount of organic substances extracted by this solvent, the dioxane had to be distilled off. The residue after distillation corresponds to the quantity of non-polar organic substances. Similarly, with the DMF extract the solid residue part is determined gravimetrically. This contains mainly non-volatile polar compounds such as humic acids and ligninsulphonic acids.

The amount of volatile substances not recorded in both extracts is about 10 per cent, according to our experience. The group of polar compounds mostly comprises organic acids. To record this acid group of chemical substances, MAIER (1975) proposed a simple method of determination.

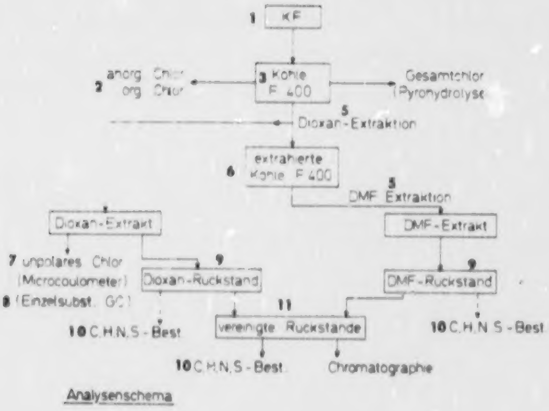

1 KF
3 Kohle F 400
2 anorg. Chlor
org. Chlor
Gesamtchlor (Pyrohydrolyse
5 Dioxan-Extraktion
6 extrahierte Kohle F 400
5 DMF Extraktion
Dioxan-Extrakt
DMF-Extrakt
7 unpolares Chlor (Microcoulometer)
8 (Einzelsubst. GC)
9 Dioxan-Rückstand
9 DMF-Rückstand
11 vereinigte Rückstände
10 C.H.N.S-Best.
10 C.H.N.S-Best.
10 C.H.N.S-Best.
Chromatographie
Analysenschema

Fig. 2: Schematic layout of analytical procedure

1 KF: control filter
2 anorg. Chlor: inorganic chloride
2 organ. Chlor: organic chlorine
3 Kohle F 400: activated carbon (Filtrasorb 400)
4 Gesamtchlor (pyrohydrolyse): total chlorine (pyrohydrolysis)
5 Extraktion. extraction
6 extrahiert: extracted
7 Unpolares Chlor: non-polar organo chlorine
8 Einzelsubstanz GC: single compounds, gas chromatograph
9 Rückstand: residue
10 C,H,N,S.-Best.: C,H,N,S, determination
11 vereinigte Rückstände: combined residue

Because the titration of extremely weak acids in a water solution is not possible, a water-free solvent with a p_{KS}-value > 16 must be taken. DMF is employed as a solvent, and in this case becomes both extraction agent and solvent. For titration of the acids potassium hydroxide in a propane-benzene solution is taken, using thymol-blue as an indicator.

Some results of these measurements are shown in Table 5 where the acid equivalents are listed in mmol/m^3 water. The increasing values from the Lake of Constance to the Lower Rhine can be seen as well as the decreasing acid equivalents in bank- and ground-filtration.

In addition, with this method it can be shown that different types of activated carbon show different properties in the adsorption of polar acid compounds.

Table 5: Acid equivalents at different sampling stations: mmol KOH/m^3 water

Sampling station	acid equivalent
Lake of Constance	3.4
Rhine at Basel	5.9
Basel, after ground water filtr.	1.9
Rhine at Cologne	18.9
Cologne, bank filtrate	6.8
Rhine at Duisburg	19.0
Duisburg, bank filtrate	12.7
Esch, after ground water filtr.	12.2
Weiler, after ground water filtr.	4.3
Donau at Leipheim	6.1
Neckar at Ludwigsburg	10.4
Fulda at Kassel	9.1
Weser at Bremen	11.4
Ground water, Grenzach	1.8

Table 6: Molar acid numbers in water works filters.

activ. carb.	Ds	SZm above	SZm below	percent of increase or decrease
F 300	64	3.14	3.33	+6
F 300	61	2.08	3.16	-6
F 300	79	2.36	2.17	-8
F 300	37	2.48	2.46	-0.8
LSS	34	3.73	4.46	-20
LSS	34	3.12	4.28	+37
LSS	35	3.10	4.44	+43
LSS	60	2.02	4.01	+49

Ds = m^3/kg; SZm above = molar acid number, upper layer
SZm below = molar acid number, lower layer

This fact is shown in Table 6 where the distribution of acids in water works activated carbon filters is shown. It was possible to prove that activated carbon with less affinity to organic acids, such as LSS, show in the lower part of the filter much more accumulation of acid substances because of displacement by non-polar compounds from the upper to the lower part of the filter. F 300, however, givesa relative equal (symmetric) distribution through the whole height of the filter. This behaviour, characteristic for polar compounds, is reversed in the use of non-polar chlorinated hydrocarbons, as can be seen in the results to be discussed later.

Table 7 shows some analogous measurements at two otherwater works filters, filled with the same types of activated carbon.

Table 7: Molar acid numbers of control filters before and after water works filters

F 400	KF	before GF	SZm = 3.44	
F 300	GF	above	SZm = 2.98	
	GF	below	SZm = 3.16	+ 6 %
F 400	KF	after GF	SZm = 2.71	-21 %
F 400	KF	before GF	SZm = 2.67	
LSS	GF	above	SZm = 3.73	
	GF	below	SZm = 4.46	+20 %
F 400	KF	after GF	SZm = 3.34	+25 %

KF = control filter
GF = water works filter
SZm = mmol KOH/g extract
(molar acid number)

At this plant, however, measurements are carried out with control filters too, one being installed before and one after the water works filter. The resulting data showed that the activated carbon type F 300 adsorbs organic acids, whereas the filtrate of the water works filter, containing type LSS, shows much higher acid concentration than in the water supply. In this case primary adsorbed acids are displaced from the activated carbon by less polar substances such as organic chlorine compounds.

Among other things, the group of polar substances includes the organic sulphur compounds (SCHWEER et al, 1975). Of these, those with an aromatic group are preferably adsorbed onto activated carbon. Because the organic sulphur compounds commonly are of low volatility, the DMF extract is used for their determination.

Table 8: Proportional comparison of organic bound sulphur and organic bound chlorine in activated carbon control filters at different sampling stations

Sampling Station	adsorb.org. substances mg/m^3	sulphur %	chlorine %	org. bound sulphur mg/m^3	org. bound chlorine mg/m^3
Lake of Constance	1300	0.4	0.5	5	6
Rhine at Basel	2900	1.5	2.3	44	67
Rhine at Duisburg	6500	5.1	2.3	332	150
Donau at Leipheim	2000	1.0	1.2	20	24
Neckar at Heilbronn	4600	1.4	1.2	64	55
Fuda at Kassel	4100	0.6	0.3	25	12
Ruhr at Mülheim	3000	2.5	0.9	78	26

In this table the organic substances adsorbed by activated carbon from water and recovered by extraction are shown, the organic bound sulphur and the organic bound chlorine in one m^3 water, respectively. Along the length of the Rhine, the total amount of adsorbable organic substances is clearly increasing; at the same time the contents of sulphur and chlorine in the extraction are increasing too. The values of the river Ruhr are remarkably lower than those of the Rhine near Duisburg. In Table 8 it can be seen that the lowest values are obtained of the lake of Constance and the river Fulda. These measurements give a good indication of the pollution of surface waters, because natural waters do not contain organic chlorine or organic sulphur.

In Fig. 3 results obtained with control filters in water treatment plants at the Lower Rhine are shown.

Fig. 3: Change of the composition of organic substances during the treatment process of water from the Lower Rhine (mean values 1974)

The values are given for the Rhine, the bank filtrate and for purified water. The first column in the diagram contains the total organic substances calculated from DOC measurements, while in the second column the organic material adsorbed onto the activated carbon filter, measured as dried extract, is shown. The third column refers to the organic sulphur compounds and the fourth shows the organic chlorine compounds determined by pyrohydrolysis. The efficiency of bank filtration can be seen from the DOC and control filter measurements. Similarly, the organic sulphur compounds are considerably reduced during bank filtration. However, the organic chlorine compounds remain unaffected by bank filtration. The latter can be removed only in the activated carbon filters in the waterworks.

The widespread practical importance of chlorine- and sulphur compounds can be seen from the investigations of the filters in various waterworks. The difference in performance, as mentioned before, results from the different sorts of activated carbon. The schematic drawing in Fig. 4 shows the loadings in the upper and lower layer of two different activated carbons at the same specific throughput.

Fig. 4: Average loading of activated carbon in water works filters at the waterworks along the Lower Rhine

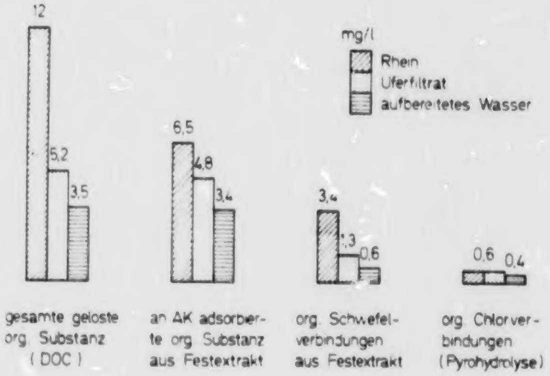


Fig. 3: Change in composition of organic substances during treatment of water from the Rhine, in the Lower Rhine (average values 1974)

Gesamte gelöste org. Substanz (DOC): total dissolved organic carbon (DOC)

an AK adsorbierte org. Substanz aus Festextrakt: activated carbon adsorbable substances as solid extract

org. Schwefelverbindungen: organic sulphur compounds as solid extract

org. Chlorverbindungen : organo-chloro compounds

Rhein: Rhine
Uferfiltrat: bank filtrate
aufbereitetes Wasser: treated water

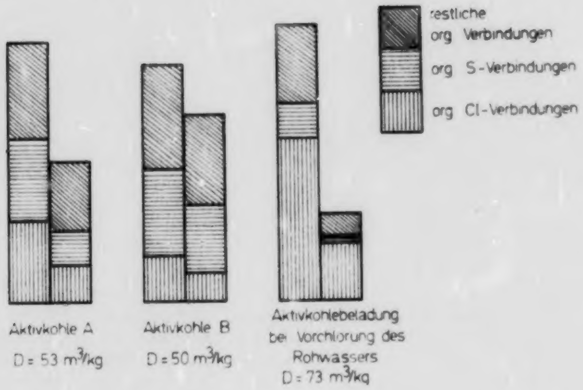


Fig. 4: Average loadings of activated carbon in waterworks on the Lower Rhine

restliche org. Verbindungen: remaining organic compounds
org. S-Verbindungen: organic sulphur compounds
org. Cl-Verbindungen: organo-chloro compounds
Aktivkohlebeladung bei Vorchlorung des Rohwassers:
Loading on activated carbon after pre-chlorination of raw water

The results on the left are the loading of the upper layer, and on the right those of the lower layer, resp. Activated carbon A has a great affinity to organic hydrocarbons, which enrich especially in the upper layer, while activated carbon B shows better adsorption of the total organic substance and consequently of more polar organic sulphur compounds. The third schematic drawing shows an activated carbon which was used in the purification of raw water, subjected to a pre-chlorination. Since the content of humic substances was relatively high, the loading of chlorinated hydrocarbons is considerably greater and as a result exceeds the common quantity of 20 per cent of the total loading.

For completeness' sake it ought to be mentioned that the control-filter method enables one to show the effect of chlorination on the formation of organic chlorine compounds. Some typical examples of these investigations are shown in Table 9.

Table 9: Increase of organo-chloro compounds as a result of chlorination of raw waters, total organic bound chlorine and non-polar bound chlorine in µg/l

Surface water	bank filtrate	after chlorination	after activated carbon
19/5	-	128/22	71/2
-	90/19	212/22	65/10
11/10	-	237/49	171/33
173/29	79/29	343/24	194/22
135/18	83/9	ozonization	32/4
53/12	-	ground filtration	30/8
13/1 $\frac{\text{1 mg Cl}}{\text{per litre}}$ 34/3 $\frac{\text{ground}}{\text{filtr.}}$ 5/0 $\frac{\text{0.5 mg Cl}}{\text{per litre}}$ 10/1			

Without regarding details, it can be seen that especially breakpoint chlorination results in the formation of a large amount of organic chlorine compounds. The last example in Table 9 shows that a considerable number of chlorine compounds were not resistant to the purifying process. In this case, chlorination was carried out in a multimedia filter before the removal of solids. This was followed by ground filtration, which decreased the concentration of organic bound chlorine; but the final safety chlorination caused a small increase of these compounds.

The numbers before the diagonal line in Table 9 refer to the total organic bound chlorine, those following it to the non-polar organic chlorine. For comparison, the results from waterworks which do not use chlorination but ozonization and ground filtration are shown in the middle section of the Table. In this case, there is an effective decrease of the organic chlorine content of raw water.

Information on the mechanism of the formation of chlorinated hydrocarbons as a consequence of superchlorination of water is given by ROOK (1974 and 1975), BELLAR et al (1974) and ROBECK (1975).

The methods used in the control filter investigations may also be employed in the examination of the efficiency of waterworks filters. For this purpose, samples of activated carbon were taken from the upper and lower layers of the water works filters (KÜHN, FUCHS, 1975).

In the following section the statistical evaluation of a large amount of data from a waterworks filter is given. The data refer to one waterworks at the Lower Rhine, since the evaluation of different types of activated carbon is only possible on the same raw water. To characterize two types of activated carbon the total loading has been measured and broken-down into its dioxane and DMF extract fractions. In addition, the loading of polar and non-polar organo-chloro compounds was measured. The data shown are average values of the loading of the upper and lower section of the filter. These values are related to the specific water throughput. Because of the scatter in the data, to be expected in an industrial plant, mean values have been calculated. The resulting data are shown in Fig. 5.

Fig. 5.

The following conclusion can be drawn: Both types of activated carbon show a decrease in their total loading after a specific flow rate of 70 m^3/h is reached, although the maximum is reached somewhat earlier with LSS than with F 300. At maximum loading, F 300 contains about 6.5 per cent by weight of organic material and LSS about 5.5 per cent. The subsequent decrease in loading after reaching the maximum value may be partially due to biological processes taking place on the carbon.

However, the amount of dioxane extract shows a reverse tendency, here LSS has a larger capacity than F 300. In addition, it may be seen that the decrease in dioxane-extractable material occurs earlier than with the humic compounds, which are present at a much higher concentration, and which hinder the adsorption of non-polar substances.

The general conclusion to be drawn is that these activated carbons have an optimum specific throughput of about 50 m^3/kg of carbon.

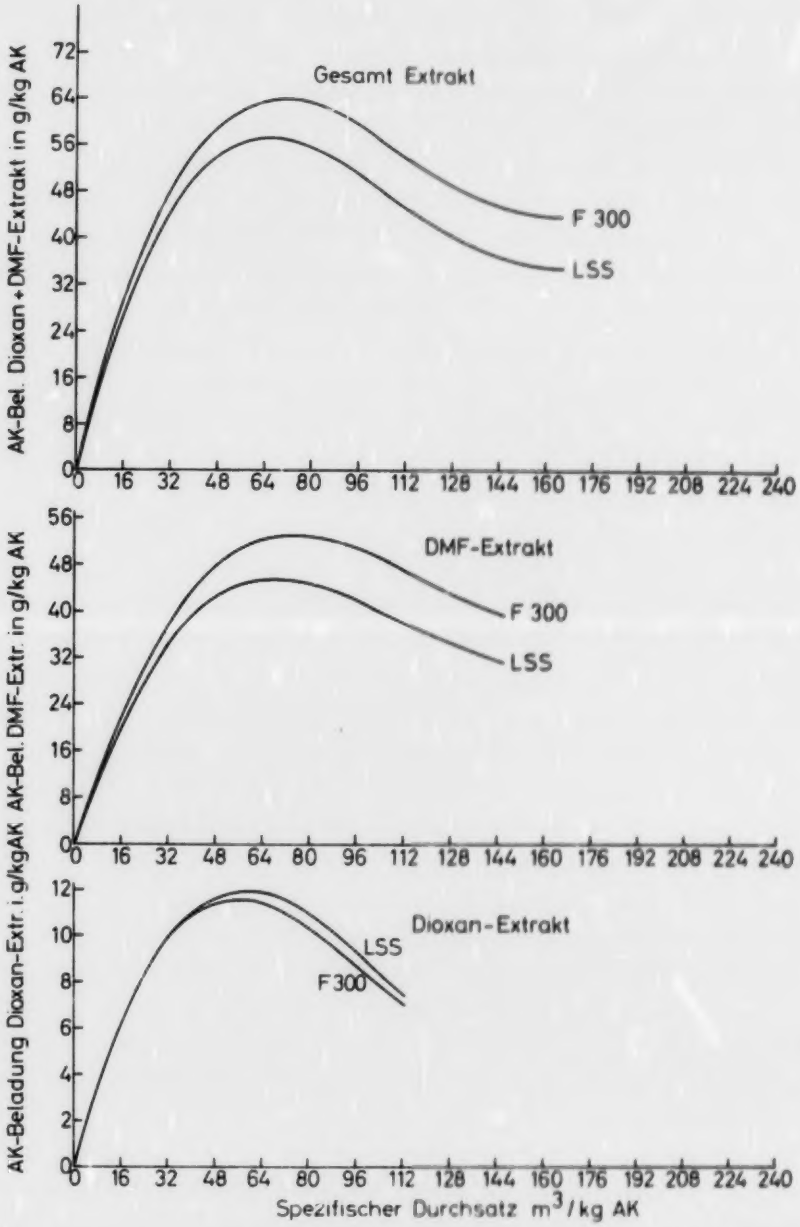


Fig. 5: Waterworks filter with LS Supra and F 300 activated carbons. Dependence of loading on specific throughput

Gesamtextrakt: total extract

DMF: DMF

Beladung: loading

Spezifischer Durchsatz: specific throughput

The corresponding curves for organo-chloro compounds are shown in Fig. 6.

Fig. 6

The maximum loading of LSS was about 3.8 g/kg of activated carbon while F 300 had a value of about 2.8 g/kg. These figures correspond to about 7 per cent of the total organic loading for LSS and about 5 per cent for F 300. However, the differences in the affinities of the two carbons for non-polar organo-chloro compounds are much more striking. The average value obtained for LSS was approximately 0.88 g/kg (1.5 per cent of the total organic loading) and 0.65 g/kg for F 300 (1 per cent of the total organic loading). Thus it may be seen that LSS is able to adsorb more non-polar organo-chloro compounds than F 300; on the contrary, the latter activated carbon has a greater affinity for high molecular weight aromatic compounds. This may be seen in its ability to give a higher UV removal (KÖLLE, SONTHEIMER, 1973; KÖLLE, SONTHEIMER, STIEGLITZ, 1975).

The inorganic chloride loading is shown in the bottom section of Fig. 6. This data was determined by nitrate exchange on the activated carbon (KÜHN, SONTHEIMER, 1974). Since raw water contains a far greater quantity of chloride than organo-chloro compounds, it is to be expected that the inorganic chloride is also adsorbed. Comparing the data, it may be seen that the chloride adsorption is the same order of magnitude as the adsorption of non-polar organo-chloro compounds, lying between 0.5 and 0.9 g/kg of activated carbon.

In the case of the more lightly loaded activated carbon in the control filter, the chloride loading often may be more than 50 per cent of the total chlorine loading.

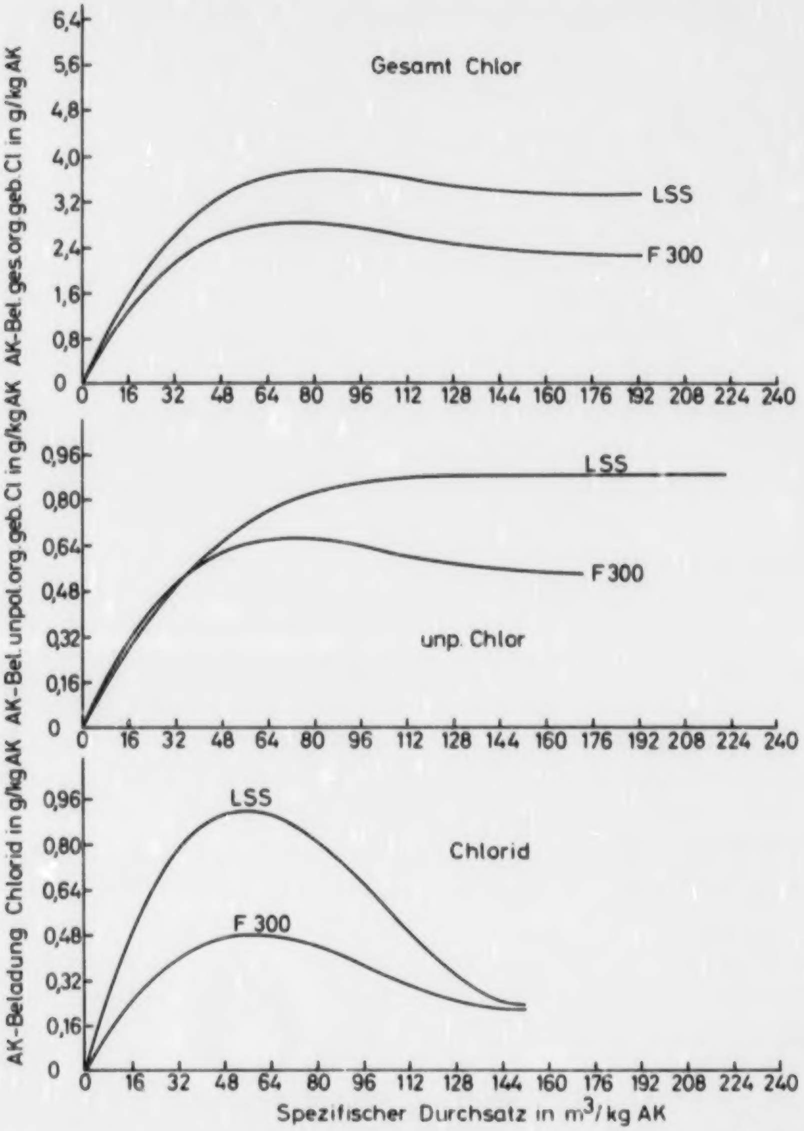


Fig. 6: Waterworks filter with LS Supra and F 300 activated carbons. Dependence of loading and specific throughput

Gesamtchlor: total chlorine

unp. Chlor: non-polar organic chlorine

Chlorid: chloride

Beladung: loading

Spezifischer Durchsatz: specific throughput

The chlorine loading drops if other readily adsorbable substances are present. This presents the possibility of obtaining a rapid indication of the appropriate loading. Analogous effects can be seen when the chloride loading in the upper and lower sections of the filter are examined. It is always found that the lower section is more highly loaded than the upper section. However, this will not be examined in further detail as it is of more academic interest than practical importance. However, it is important that by means of a simple chloride determination it is possible to obtain a rough indication of the degree of loading of the carbon. This method is practicable, provided the chloride concentration in the water remains in the same concentration range.

Similar investigations on other waterworks filters are shown in the upper section of Fig. 7. From these results the following conclusions can be drawn:

1) The percentage of dioxane-extractable material decreases with increasing throughput.

2) With throughputs of more than 50 m^3/kg the loadings on LSS and F 300 remain constant under the existing water composition.

3) Norit activated carbon shows the highest increasing in loading even at high throughputs, with organic material of a polar nature.

From the data in the lower section of Fig. 7 the following conclusions can be drawn:

1) In the case of activated carbons with strongaffinities for polar substances such as F 300 or Norit, the loading of organo-chloro compounds increases only in the lower section of the filters at higher throughputs.

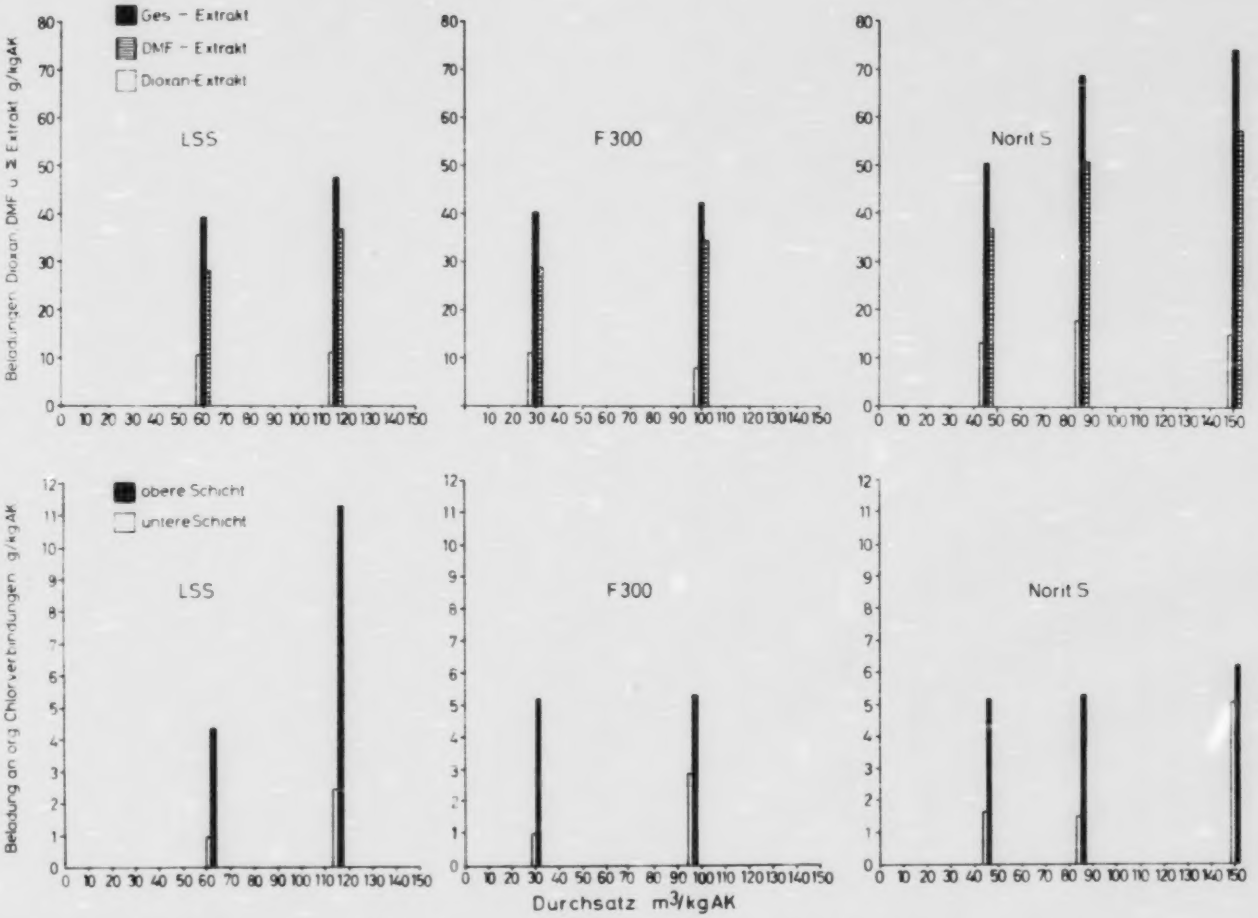


Fig. 7: Dependence of loading on specific throughput for different activated carbons

Ges.-Extrakt: total extract

Obere Schicht: upper section

untere Schicht: lower section

Beladung: loading

Durchsatz: throughput

2) LSS has the highest capacity for organo-chloro compounds in the upper section also at the higher throughputs while still retaining available capacity in the lower section.

3) Activated carbon with a high affinity for organo-chloro compounds, such as LSS, generally has a small adsorption capacity for higher molecular weight organic substances.

It should be pointed out that these conclusions may be valid only in this particular instance and should not be taken as the general case, since different waters show different behaviour with the same carbons.

It may be concluded by saying that the above outlined methods provide a good means of investigating the properties of activated carbons,and their application may contribute to improve the use of activated carbons in waterworks.

CONSIDERATIONS ON THE OPTIMIZATION OF ACTIVATED CARBON USE IN WATERWORKS

by H. Sontheimer

The reports on practical experience with activated carbon filters in waterworks show how different the results and optimum solutions may be in practice. Most important in this respect is the pretreatment prior to the activated carbon filters. As a supplement to the reports by POGGENBURG, HEYMANN, SCHEIDTMANN, JANATA and VAN LIER, some additional considerations are presented below.

Firstly, it must be stressed once more that specifying the degree of purification to be achieved is of utmost importance for determining the choice of carbon and the optimization of the whole treatment process. It is therefore most important that a suitable analytical method is proposed for the control of the activated carbon filter.

About 20 years ago, when activated carbon filters were used for the first time in Western Germany for dechlorination and further improvement of water quality, the analytical methods were relatively simple and only the odour threshold number was measured regularly (HOLLUTA 1960). The method of measurement may have been subjective but, since it was always carried out in the waterworks by the same person, provided satisfactory and comparable data. By measuring the threshold number at different heights in the filter it was also possible to obtain some indication of the expected running time of the filter.

Today it is still necessary to remove taste and odour with activated carbon filters, but this task is not of primary importance now because it has been shown many times that taste and odour are fully removed when the filter process is orientated towards lowering the total concentration of dissolved organic carbon or towards an extensive removal of organochloro compounds. However, there are considerable differences in the effectiveness of different activated carbons, depending on the analytical method used, as illustrated in the following Table.

Table 1: Comparison of different activated carbon types according to different parameters

DMF-extract solution (Langenau waterworks) spiked with organo-chloro compounds (raw water used for testing)

D O C	119.9 mg/l
C O D	254.5 mg/l
U V (250 nm)	1.32
Org. Cl	14.8 mg/l
Lindane	0.6 mg/l

Residual concentrations after 40 hours at 5 g/l activated carbon dosage

Carbon type	DOC	COD	UV	Org.Cl	Lindane
L S	34.7	42.9	0.050	11.2	0.009
LSS n	25.6	19.2	0.015	11.9	0.002
LSS a	28.4	25.3	0.010	22.0	0.002
C 2	29.2	30.3	0.095	10.9	0.002
F 400	24.8	23.2	<0.010	11.9	0.001
B 10	21.0	14.6	0.040	14.3	0.001

In this Table the results of several experiments are presented in which a number of different types of activated carbon were used in a solution of a carbon extract from the Langenau waterworks, spiked with different organo-chloro compounds. After adsorption a variety of parameters have been measured. These included sum parameters, such as the DOC and the COD, and group parameters such as UV extinction and the organic chlorine concentration. Additionally, in this instance a single compound, Lindane, was also analysed.

It may be clearly seen from the results that, depending on the analytical method, no particular carbon is shown to be the most effective. This means that the judgement on activated carbons is largely dependent on the analytical method and the evaluation criteria. More detailed discussions on the problems connected with testing procedures for activated carbon are presented in subsequent papers.

However, it should be noted that the choice of testing parameters has a marked influence on the treatment conditions. It has been shown many times that the adsorption of odour is considerably faster than the adsorption of many other organic substances. As long as the removal of taste and odour were the only considerations, it was possible to use filter velocities of 30 m/h without deleterious effects. However, a high degree of removal of all organo-chloro compounds requires longer contact times, and under these circumstances the effect of competitive adsorption must also be considered (WEBER and MORRIES 1964, KOPPE 1967).

Where high degrees of removal are required, the optimization of the pretreatment processes is of increasing importance, since it not only has an effect on the removal of odour compounds but also on the removal of all contaminants. Thus the different pretreatments used at each waterworks require individual carbon evaluation procedures. In addition to the papers of HEYMANN and SCHEIDTMANN some recent results obtained from the testing of water from the river Ruhr, which clearly illustrate the variety of different pretreatment processes, are described in the following chapters (NOLTE, VOLLMER 1975). There the question arose whether it might be possible to obtain very low residual amounts of organics in the processed water, using a suitable pretreatment prior to adsorption. Therefore, the adsorption capacity after various pretreatments of Ruhr water was examined, the results of which are presented in Fig. 1.

Fig. 1: Carbon consumption required to achieve a set DOC in pretreated water from the river Ruhr

In this Figure the carbon consumption required to obtain a certain DOC level is presented, which was calculated from equilibrium measurements obtained for two activated carbons. It can be seen that the carbon dosage, which is necessary to obtain a certain residual organic level, is lowered by additional ozone treatment. It is interesting that an identical effect can be obtained if chlorine is used in place of ozone. This procedure, however, has the disadvantage of causing a very rapid loading of the filter with organo-chloro compounds, resulting in a more frequent filter regeneration. Also, it was found that a total removal of organic material of more than 80 to 90 per cent was necessary to remove all organo-chloro compounds formed through chlorination. Furthermore, it may be seen from Fig. 1 that 10 g/m^3 chlorine produce about the same result as 3 g/m^3 ozone. An additional result was that greater effectiveness of the activated carbon can be obtained after ozone application followed by flocculation. This results in the partial removal of the polar substances formed during ozonization.

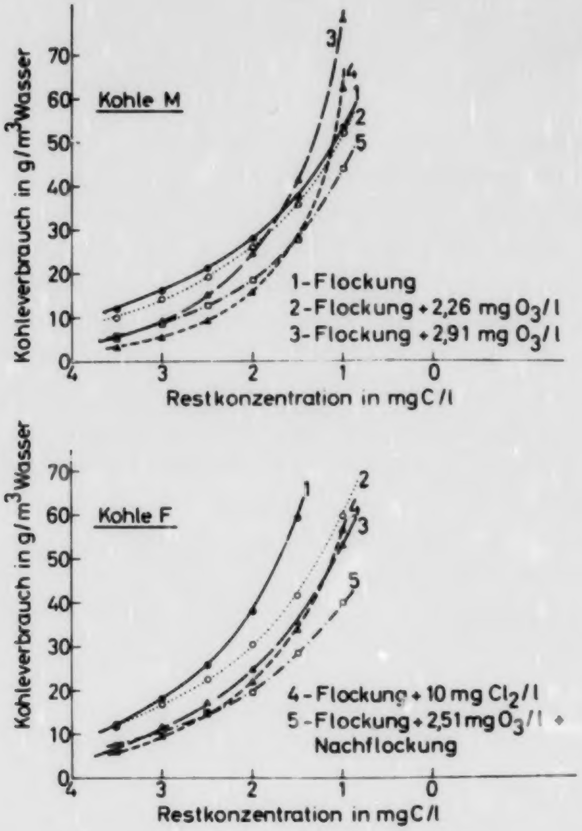


Fig. 1:

Kohleverbrauch in g/m^3 Wasser: carbon consumption in g/m^3 water

Flockung: flocculation

Restkonzentration in mg C/l: residual concentration in mg C/l

Nachflockung: after-flocculation

From the results presented it may be seen that the type of pretreatment determines also which of the two carbons shows a better effectiveness, that is to say, a lower consumption of carbon to reach the same residual concentration of organic material.

In the presented figures the carbon consumption has been calculated from equilibrium measurements. If one also considers the adsorption kinetics and the different effects of various pretreatments on biodegradation in the carbon filter, together with plant-to-plant and season-to-season variations of different contaminants, it becomes obvious that it is not possible to set generally valid rules for the optimization of the activated carbon treatment and the preceding pretreatment process.

Judging by the experience gained so far, there seems to be no other way than to carry out in each individual case suitable parameter studies on existing plants or test plants, and to ascertain the specific dependencies. Thus different results are obtained in each individual case, which is to be expected, considering the different combinations of organic compounds. Nevertheless, one may draw the following general conclusions regarding the optimization of an activated carbon treatment:

1) Optimum activated carbon use requires regular process controls, whilst at the same time various parameters have to be checked.

2) In general, each change within the treatment process before the carbon filter has both advantages and disadvantages. Thus, the use of ozone may improve the adsorption equilibria as well as the biological effectiveness of the activated carbon, but may impair the adsorption kinetics. Similar problems arise with most treatment processes.

3) Only in rare cases experience gained at one waterworks may be transferred without modification to another works. In each case it is essential to check the consequences of certain measures, and only then may conclusions be drawn from the results.

4) It appears that the best optimization is achieved by an exact control of the plant performance in such a way that one can draw final conclusions from the results, taking into account the experience gained at other works. This type of procedure has proved successful during the past five years.

COMPARATIVE ASSESSMENT OF ADSORBENTS

by

J. Klein, Essen

Introduction

For decades, adsorbents have brought the solution to problems of various kind, as e.g. in the field of air and water purification, gas drying, solvent recovery etc.: activated carbon e.g. is used for gas and vapour adsorption, as decoloration agent, in respiratory apparatus, for water treatment, medical purposes, batteries, and as catalyst or catalyst carrier. Aluminium oxide is used mostly for drying purposes, as catalyst or catalyst carrier, but may also be used for adsorption and precipitation of liquid-phase polar matter. Silica gel is mainly used for drying purposes or as catalyst or catalyst carrier. Molecular sieves are used for drying and purification of gases and for hydrocarbon recovery.

This variety of applications requires a characterization of the individual adsorbents and necessitates specification of the individual product with respect to the process applied.

For this reason, research and development work was carried out over many years in order to establish suitable testing methods, but due to the very specific characteristics of the individual adsorbents, the respective testing methods exhibit correspondingly very specific features. However, some of the testing methods could be standardized. Thus, e.g., DIN 19 603 "Technische Lieferbedingungen für Aktivkohlen zur Wasseraufbereitung" (Technical supply conditions for activated carbon for water treatment) contains determination procedures for bulk density, water content, phenol adsorption capacity, and dechlorination capacity. So, parameters are quoted which possibly are useful for assessment of the adsorbent and which may be complemented by any further parameters required.

For determination of the adsorption capacity or the adsorption performance, however, only very few standard methods are available, but a variety of specific bases of evaluation developed by the manufacturers or users of adsorbents is partly used outside their specific field of application. In the present paper, some assessment methods for adsorbents will be explained, and proposals will be submitted for comparative evaluation of the methods in order to assess their value for operation practice.

Description of test methods

The most important characteristics for adsorption are size and state of surface and the pore structure. The term "pores" stands for the hollow spaces in solid-state particles accessible to the adsorptive, (adsorbate) subdivided according to IUPAC standard into macropores (d > 25o AE), mesopores (25o AE > d > 2o AE), micropores (2o AE > d > 4 AE) and submicropores (d < 4 AE). The walls of these hollow spaces constitute the inner surface, generally determined according to Brunauer, Emmett and Teller (BET) by gas adsorption (see DIN 66 131). Apart from the so determined size of surface, its chemical constitution is of specific importance, characterized in a simple way by differences in the affinity between adsorbent and different classes of adsorptives. Data on the pore structure may be obtained from the distribution of pore radii to be calculated, e.g., for radii > 1oo AE by Hg-porosimetry and for smaller radii (micropores), e.g., on the basis of benzene or steam adsorption.

These three properties of adsorbents always have a combined influence on the adsorption process as may be seen from the adsorption isotherms of four different adsorbents, with water and benzene used as adsorptive (see Figure 1). The

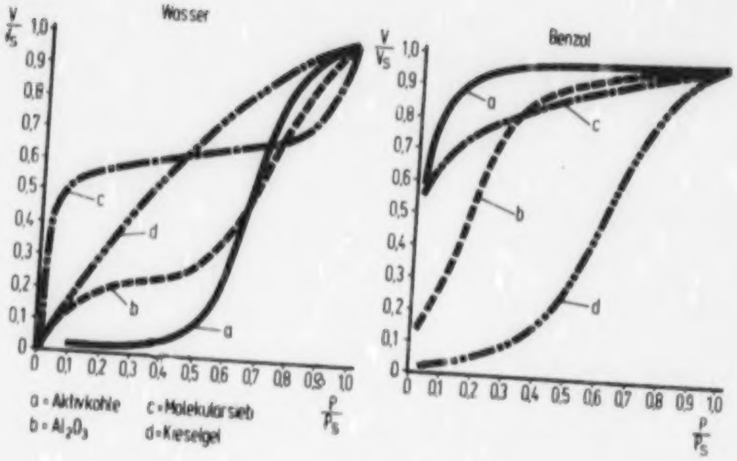


Figure 1: Adsorption isotherms of different adsorbents

Water

a) activated carbon

b) Al_2O_3

Benzene

c) molecular sieve

d) silica gel

relative adsorbate volume V/V_s is plotted as a function of the relative partial pressure of the adsorptive p/p_s.

Water as adsorptive may be considered first: In case of the zeolitic molecular sieve (curve c) the load increases sharply, already at very low partial pressure, reaches saturation, followed at $p/p_s \sim 0.8$ by further increase. This isotherme corresponds to type II of the Brunauer classification. The behaviour of Al_2O_3 (curve b) towards water is similar. However, in this case a considerably slower increase of load at low partial pressure is stated. This type of isotherm (type II) indicates the existence of two different adsorption mechanisms, i.e. two different pore systems. In case of silica gel (curve d) a nearly linear course is obtained fulfilling Henry's law over a large range of partial pressures.This curve, however, may be understood as a limit case of isotherm type I. In case of activated carbon (curve a) it is isotherm type V we are dealing with, i.e. at low partial pressures only very few active centres for adsorption are available and, above $p/p_s \sim 0.5$, suddenly capillar condensation starts. Adsorption of non-polar benzene looks quite different. In this case, adsorption by activated carbon takes places according to isotherm type I. The molecular sieve and Al_2O_3 behave similarly, however at lower p/p_s-values load is definitely smaller. Silica gel hardly adsorbs at low p/p_s-values and corresponds to isotherm type V.

These results may be understood as follows: according to theoretical deduction,a steep increase of load at low partial pressures is caused by high energy of interaction between adsorptive and adsorbent, as applies to isotherm type I and partly to type II. The isotherm type V, however, is based on interaction between adsorptive and adsorbent being considerably less compared with interaction among the molecules of the adsorptive. In case of water adsorption, therefore, we may derive from the isotherms recorded that the molecular sieve shows the highest interaction between adsorptive and adsorbent, followed by silica gel, Al_2O_3 and activated carbon. In case of benzene adsorption interaction is highest with activated carbon and lowest with silica gel. Substances exhibiting high interaction with water are called hydrophillic and those with high interaction with non-polar aromatic matter are called hydrophobic.

Quantitatively, a hydrophobia quotient may be defined as the ratio of interaction energy of water and benzene to the adsorbent; determination may be carried out experimentally by measuring the heat of immersion.

Since all adsorbents may be characterized comparably by means of adsorption isotherms, the present article will be confined to activated carbon as adsorbent. Described are the test methods for the five adsorptives normally used, i.e. phenol, iodine, methylene blue, TBS (tetra propylene benzene sulphonate) and molasses.

Phenol adsorption

Phenol adsorption was initially used for determining the capacity of activated carbon to remove aromatical matter. Two standardized methods exist: DIN 19 6o3 dealing with determination of the isotherm of ground activated carbon using an initial concentration of lo mg/l of phenol ($c/c_S \sim$ o.oool), whereas according to AWWA instructions the phenol desorption by a layer of granulated activated carbon, saturated by a phenol solution (5ooo mg/l $\hat{=}$ c/c_S = o.o5) is determined. Figure 2 shows for comparison the results obtained by both methods for activated carbon qualities of different degrees of activation. From the mere phenomenological point of view, we may state that the phenol load increases initially with the degree of activation, reaches a peak and then decreases. This may be explained by the change in the pore structure of activated carbon during the activation process, as has been explained previously by Jüntgen.

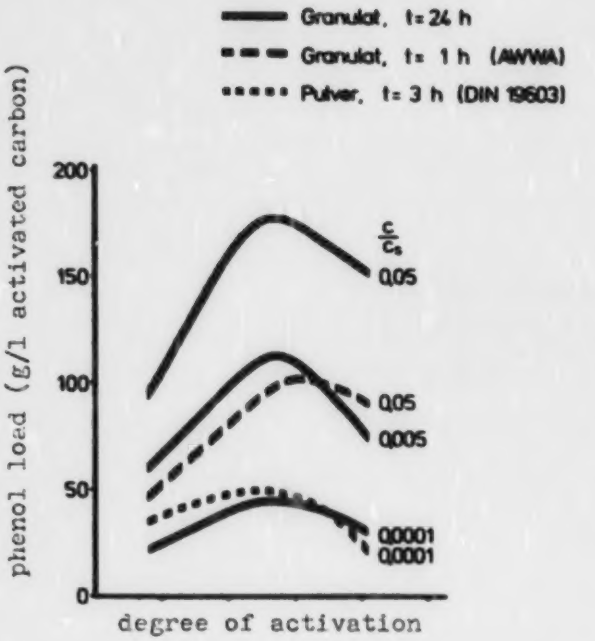


Figure 2: Characterization of the adsorption capacity in aqueous solution

___ granualated material (matter) t = 24 h
--- " " t = 1 h (AWWA)
... " " t = 3 h (DIN 19 6o3)

Using the AWWA regulations, we obtain the upper dark-line curve for a pre-determined contact period of one hour and an initial concentration of c/c_S = o.o5 for a cylindrically formed carbon. With a contact period of 24 hours, sufficient for obtaining the equilibrium load, the upper curve is obtained for the same series of activated carbon quality at c/c_S = o.o5. The middle full-line curve indicates the equilibrium load at c/c_S = o.oo5. It may be seen that the load obtained according to AWWA instruction is by 5o % smaller than the equilibrium load and corresponds to the one obtained at equilibrium for an initial concentration which is by lo times smaller. The fact that the dash-line curve shifts to higher degrees of activation is due to the diffusion effects in the small-diameter pores.

The result of DIN instruction using powder-fine activated carbon corresponds approximately, at identical initial concentration, to the equilibrium load. The smaller grain size creates new active centers entailing higher load at lower degrees of activation, but favourizes also the adsorption kinetics so that equilibrium is obtained already after three hours.

Determination of iodine number

The iodine number is defined as the quantity of iodine in mg adsorbed by 1 g of activated carbon, the residual concentration of the iodine solution being o.o2 normal. There are several instructions, e.g. by AWWA and PPC, according to which the ground activated carbon is vibrated over 3o seconds with a 0.1 n iodine solution (c/c_S = o.8) and a load value for a residual concentration of o.o2 n (c/c_S = o.16) is taken as the iodine number.

Iodine is found in aqueous solution as I_2 molecule which is of similar size as the benzene molecule. Therefore, in Figure 3 the iodine adsorption from a liquid phase is compared to benzene adsorption from the gaseous phase at equal external

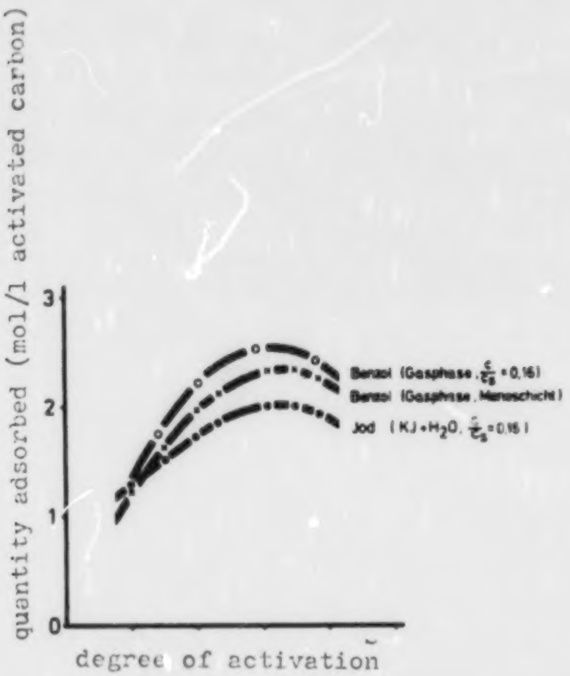


Figure 3: Characterization of the inner surface

benzene (gaseous phase $\frac{c}{c_S}$ = 0.16)

benzene (gaseous phase, mono-layer)
iodine (KJ + H_2O $\frac{c}{c_S}$ = 0.016)

concentration c/c_S = o.16 . The upper curve applies to benzene, the lower one to iodine. When evaluating the benzene isotherm according to BET we obtain the mono-layer load (see the middle curve on Figure 3). Supposing the same space requirement for the iodine molecule and the benzene molecule, the decrease of the idone values, above all in case of large-pore products, may be explained by the simultaneous adsorption of water molecules or of separated ions. It may be seen that the iodine figure moves in parallel to the benzene-determined surface so that probably it can be regarded as effective surface for non-polar matters in aqueous phase.

Methylene-blue adsorption

The volume of a o.15% solution in ml,decoloured by loo mg of activated carbon within 5 minutes,is the titration standard for methylene-blue according to DAB instruction . For this method, a residual concentration cannot be determined exactly so that the isotherm value cannot be defined exactly either.

Figure 4 shows the methylene-blue load for activated carbon qualities of different degrees of activation characterized here by the iodine number according to the method described **before** Adsorption of the compact methylene-blue molecule starts at an iodine number > 5oo. The stepwise course of the adsorption curve is due to the necessary pore size of 15 AE being reached from a certain degree of activation onwards,and to the formation of smaller pores (with increasing activation) which do not retain the methylene-blue **further.**

TBS adsorption

As for phenol adsorption according to DIN 196o3 an isotherm is used for characterization. The load equilibrium of finely ground activated carbon in a solution of 2o mg of TBS/l is reached within a contact period of three hours. The residual load in per cent by weight, at a residual concentration of 1 and o.1 mg/l, is stated as TBS load (LAT-procedure No. 311). Figure 4 shows the respective load curve in comparison with methylene-blue adsorption. Obviously, the shift of the step

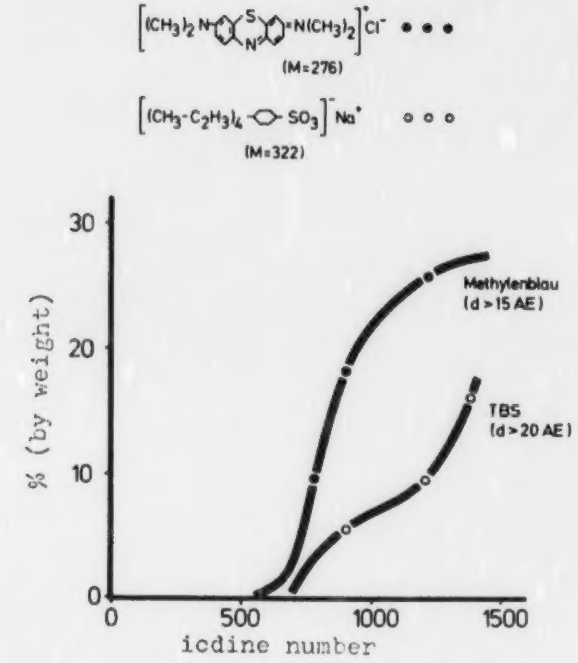


Figure 4: Adsorption on activated carbon from aqueous solution; various molecule sizes

methylene-blue (d >15 AE)

towards higher iodine numbers which means greater pore diameters may be seen. The determination of TBS load is a testing method which is of specific importance for detergent production. In unspecific use this method provides a possibility of comparison between adsorptive molecules of different size which allows conclusions with respect to pore diameters.

Molasses adsorption

For determining the decoloration capacity of activated carbon with respect to decoloration of sugar-clearing liquors, the raw material for sugar production, molasses, is used. Since many yellow colouring substances are similar to molasses colour with respect to adsorption behaviour, the molasses adsorption is considered an important test for activated carbon used in decoloration. Since the composition of the molasses solution cannot be precisely defined, the load is not stated in this test but the change in extinction, compared with the change of extinction obtained by a standard activated carbon (Carboraffin). The extinction is measured mostly by means of a Lange colorimeter. The term "molasses factor" stands for the quantitative relation of activated carbon to be tested to the activated carbon quality used as a standard at the same extinction (LAT procedure No. 228). It is known that molasses colours do not penetrate pores smaller than 28 AE.

Use of testing procedures for commercial activated carbon

In the previous chapter the adsorption of five widely used testing substances for activated carbon of different degree of activation, i.e. different pore structure but of identical chemical surface conditions, was discussed. When testing some commercial-grade activated carbons, differences in adsorption properties are found which result from different manufacturing processes and different raw material for the products.

As previously explained by Jüntgen, the raw material has a decisive influence on the pore structure. Thus, e.g., the maximum of differential pore radii distribution at the same degree of activation may be shifted by the factor 2 only by using another raw material. Figure 5 shows the methylene-blue adsorption for two degrees of activation of different raw materials; from this graph a shift of the load curve towards smaller iodine numbers may be seen. Furthermore, corresponding values for some commercial products are plotted as well. It becomes obvious that apart from some deviations the iodine numbers are in the same order of magnitude for all products. On the other hand, however, considerable differences in methylene-blue adsorption are stated. If now, for commercial products showing a comparable iodine number, a relation between methylene-blue and TBS adsorption to the molasses factor is established, it is surprisingly found that, as shown in Figure 6, with increasing molasses factor, i.e. with decreasing decoloration performance, adsorption of the smaller molecules of methylene-blue and TBS increases.

This behaviour may be explained by adsorption of the relatively large molecules of the colouring substances requiring large pores which, during manufacture, are formed to the detriment of the smaller pores which, in turn, constitute the adsorption potential for the smaller molecules.

Another correlation is found by plotting the methylene-blue adsorption against TBS adsorption (Figure 7). We first see general increase of methylene adsorption with increasing TBS adsorption for the experimental qualities of different degrees of activation (circles) and also for the selected commercial products (dots). When looking particularly at the experimental qualities, we find a kind of saturation of the methylene-blue adsorption with increasing TBS load. This confirms the hypothesis according to which the size of the molecules determines the adsorption.

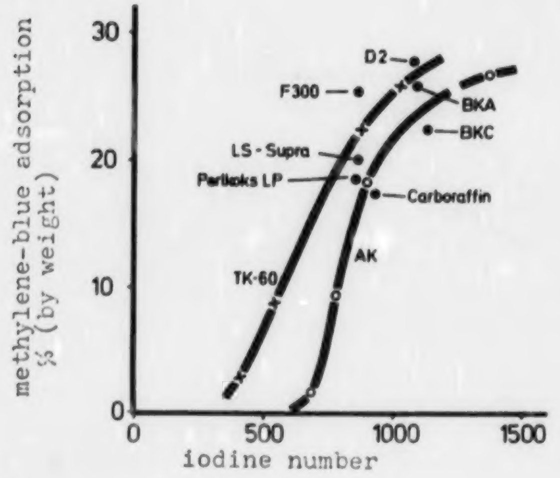


Figure 5: Methylene-blue adsorption on different activated carbon qualities

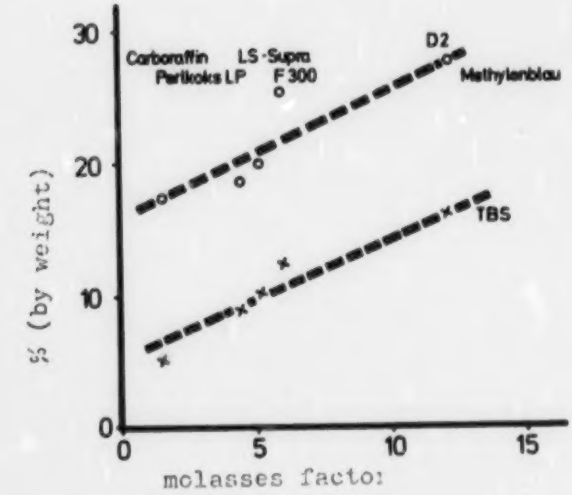


Figure 6: Correlation between molasses factor and adsorption of methylene-blue and TBS at comparable iodine number (~ 900)

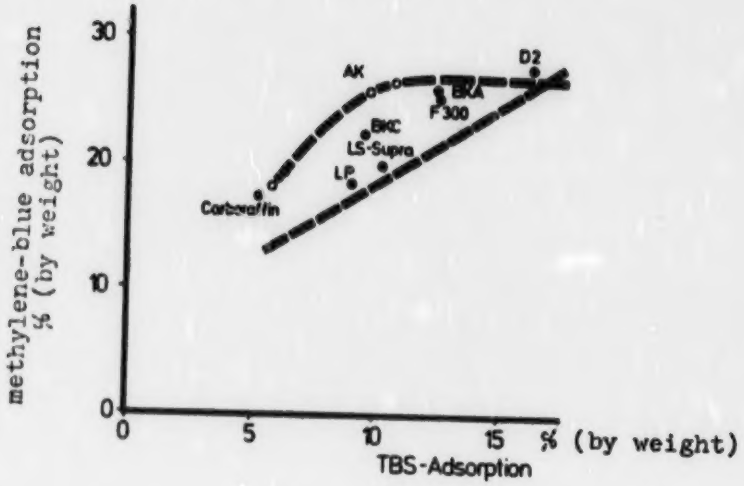


Figure 7: Correlation between methylene-blue adsorption and TBS adsorption for various activated carbon qualities

4. Evaluation with respect to operation practice

The testing methods discussed here are fairly different with respect to the value of their results. In all cases an isotherm value is indicated as characteristic figure, and this isotherm value is badly defined for methylene-blue and molasses adsorption. When using granulated matter, the test methods indicate load values which almost surely do not correspond to any equilibrium load. Despite of these deficiencies, however, it was shown that they supply certain general information on the pore structure given in the activated carbon quality under test.

Of course, the values for equilibrium load and adsorption kinetics which are of decisive influence for the break-through behaviour of an adsorption bed and which are required for the design of adsorptive purification plants are not determined by these testing methods. In addition to that, only in very few cases of industrial practice an individual substance or type of substance is contained in the water to be treated. Moreover, these waters contain complex blends of pollutants the adsorption behaviour of which cannot be simulated in reduced-scale tests.

For the solution of water treatment problems, especially for the design of adsorption plants , tests with the actual water to be treated must be carried out for determination of the adsorption isotherms and adsorption kinetics, a practice which, to some extent, has been adopted for waste-water treatment technology.

For the future, however, it will certainly be useful to find useful parameters by well- defined basic research which allows a general prediction of the adsorption behaviour for any blend of substances.

INVESTIGATIONS INTO THE CONTROL OF ACTIVATED CARBON FILTERS AT WATERWORKS

by W. Janata, Cologne

The Gas-, Electricity- and Waterworks of Cologne (GEW) have been using an activated carbon treatment plant since 1972; and a second plant is under construction.

As at other waterworks, the problems of reactivation and exchange of carbon arise also here, so that the foremost aim was to find the best parameters for determining the best time for exchange of the carbon.

In cooperation with the Engler-Bunte-Institut the following evaluation procedures were used.-The total loading on the carbon was determined using the Dioxan/DMF extraction technique developed by FUCHS (1973) while the total organic chlorine compounds were determined by pyrohydrolysis (KÜHN 1973).

Both methods provide a good indication of the extent of the total loading of the carbon when taken in conjunction with the continuous measurement of the UV extinction of the water before and after activated carbon treatment.

In order to obtain further analytical information on the method of loading of the activated carbon and especially on the extent of the important organo-chloro compounds, the gaschromatrography technique developed by PARK at the Engler-Bunte-Institut (Jahrbuch vom Wasser 1974) was also used. Slight modification of the programme procedure was found to be necessary. The procedure is shown schematically in Fig. 1.

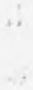
2 g moist activated carbon
+ 150 ml DMF

elution

column l = 20 cm
d = 1 cm

Eluted product
+ 600 ml H_2O
+ 30 ml n-hexane

extraction



extraction flask
V = 1 litre t = 5 min

n-hexane phase
+ sodium sulphate

drying

beaker
= 50 ml

n-hexane phase
+ n-hexane

filtration

volumetric flask
25 ml

1 - 3 µl in GLC

gaschromatrography

column: 1.8 m packed with 3 % SF 96 on Chromosorb W-

carrier gas: Ar/CH_4 (95/5) 20 ml/min

temperature programme:

$$30^\circ \xrightarrow[8\,\text{min}]{\text{Iso}} 30^\circ \xrightarrow{6^\circ/\text{min}} 240^\circ \xrightarrow[10\text{min}]{\text{Iso}} 240^\circ \rightarrow 30^\circ$$

detector: ECD puls rate 50 Jmp./sec

output: over integrator

Fig. 1: Analytical process for the determination of organochloro compounds on activated carbon

Procedure:

Separate, well-mixed samples (≈ 1 kg) of moist activated carbon were obtained from the upper and lower sections of the filter.

A 2 g sample was then placed in the elution column and the adsorbed material was then slowly eluted in portions with 150 ml of DMF. The eluted material was then mixed with 600 ml water and 30 ml n-hexane in a laboratory shaker for five minutes. The organo-chloro compounds were extracted into the n-hexane phase and, after being dried with Na_2SO_4 and filtered to remove any residual material, were analysed by GLC. (The quantitative desorption and transfer of organo-chloro compounds into the n-hexane phase was investigated by PARK, who found the recovery to be better than 95 percent.)

A 1.8 m glass column packed with 3 percent methyl-silicone SF 96 on Chromosorb W was used in the GLC. However, other silicone packings produce similar chromatograms. An ECD detector was found to be most suitable for the organo-chloro compounds.

The following temperature programme was used:

$$30^\circ \xrightarrow[8\ \text{min}]{\text{Iso}} 30^\circ \xrightarrow{6^\circ/\text{min}} 240^\circ \xrightarrow[10\ \text{min}]{\text{Iso}} 240^\circ \longrightarrow 30^\circ$$

This adjustment has the advantage of separating the readily volatile, medium and difficult-to-volatilize components. The peak area units obtained by the integrator were used for the actual evaluation.

The following illustrations show some typical results for loaded activated carbon obtained from industrial filters. The chromatograms clearly illustrate the difference in loading at the top and bottom of the column, and the adequacy of the carbon in removing the total spectrum of chloro-compounds.

Fig. 2:

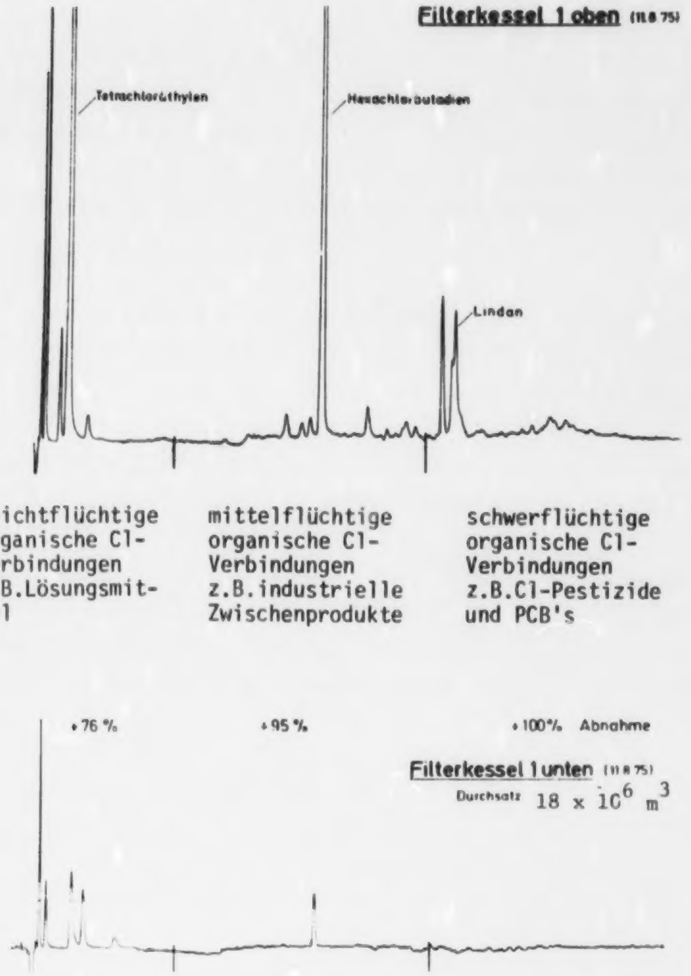


Fig. 2:

Filterkessel 1 oben: filter vessel No. 1, top

leichtflüchtige... : readily volatile organo-chloro compounds such as solvents

mittelflüchtige ...: medium volatile organo-chloro compounds such as industrial intermediate products

schwerflüchtige... : difficult-to-volatilize organo-chloro compounds such as Cl-pesticides and PCB's

Filterkessel 1 unten: filter vessel No. 1, bottom

Durchsatz: throughput

Abnahme: reduction

The tendency of the carbon at the bottom of the column to first load with the readily volatile chloro compounds can be easily seen, while the difficult to volatilize lipid-soluble and toxic chloro compounds are mostly retained in the upper layer of the filter. These substances break through relatively late, fortunately.

For evaluation, the determination of single substances was deliberately disregarded after the first tests, and instead an arbitrary classification of compounds into readily volatile, medium and difficult to volatilize was used. In this way results can be obtained more rapidly and one can see from the chromatograms that such a division is relatively easy to carry out.

Tetrachloroethylene, hexachlorobutadiene and lindane were chosen as guide compounds for each group as they have been always found in the upper layers of the filter. Then the total loading of chloro compounds from these three groups was compared in the upper and lower sections of the filter.

The practicability of this method, which requires five hours for testing one filter, was proved in that a sufficient linearity was found in the concentration range under investigation. However, Fig. 3 shows that there can be large differences amongst different filters.

From the differences in the chromatograms it can be seen that the very volatile compounds have already accummulated at the bottom of the filter bed and that therefore a breakthrough of the solvent front can be soon expected,or that this may have already occurred.

Fig. 3

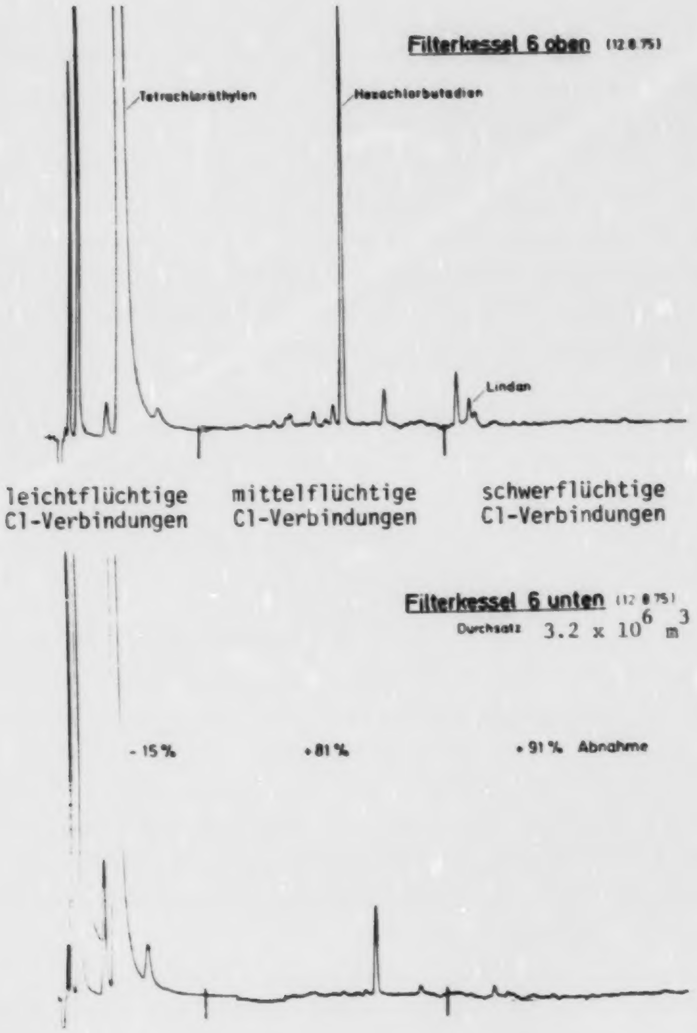


Fig. 3

Filterkessel 6, oben: Filter vessel No. 6, top
leichtflüchtige ...: readily volatile organo-chloro compounds
mittelflüchtige... : medium volatile ...
schwerflüchtige... : difficult-to-volatilize...
Abnahme: **reduction**

However, it is consoling to know that the medium and not-easily volatilized compounds are retained, which can be explained by their different adsorption properties.

The strong increase in loading of the readily volatile chloro compounds in the lower section of the filter bed provided sufficient reason to exchange the carbon immediately, although the total loading determined by DMF extraction was 62 percent lower in the bottom than in the upper layer.

Subsequently, a number of similar tests were carried out. Fig. 4 gives a general view of a test series carried out in July and August.

Fig. 4

The figures shown at the top of the diagram indicate the specific water throughput capacity (m^3/kg) in each case whilst the height of each graph represents the percentage reduction in chloro compounds through the filter.

One can see that with increasing throughput the loading of readily volatile substances increases markedly at the bottom of all filters. From this behaviour a criterion for the time for reactivation may be set.

Further investigations are planned, whereby comparative tests are to be made concurrently. However, it may be said that the above GLC method provides a rapid practical means of evaluating the effectiveness of activated carbon filters.

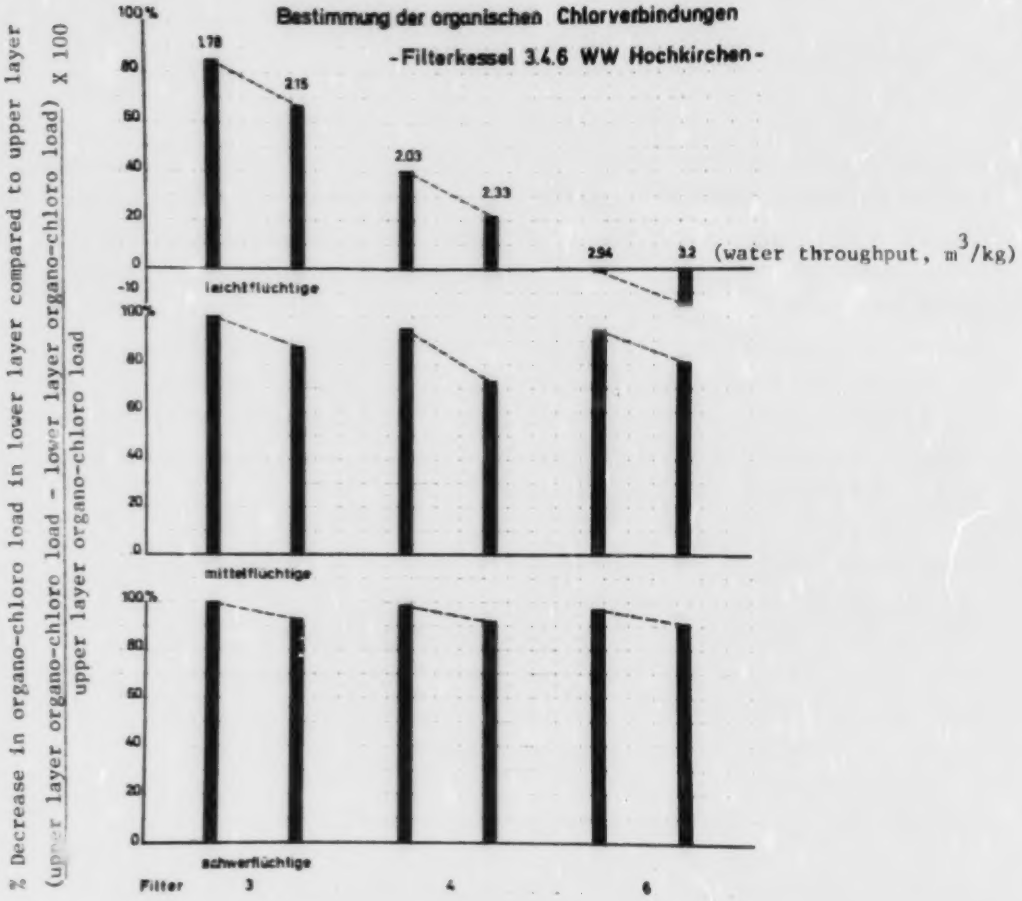


Fig. 4:

Bestimmung der organischen Chlorverbindungen: definition of organo-chloro compounds

Filterkessel 3.4.6 WW Hochkirchen: Filters 3,4,6 at Hochkirchen Waterworks
leichtfluchtige - very volatile organo-chloro compounds
mittelfluchtige - medium volatile organo-chloro compounds
schwerfluchtige - slightly volatile organo-chloro compounds

TESTING OF ACTIVATED CARBON FILTERS IN WATERWORKS

by F.J. Weißenhorn, Düsseldorf

The increasing pollution of surface waters with non-biodegradable and sometimes dangerous organic substances requires an increased use of activated carbon in water treatment. On account of the large spectrum of dissolved organics which, from an analytical point of view, are present in comparatively small concentrations, and on account of the necessity to eliminate these compounds as far as possible, the activated carbon used in waterworks has to meet especially high standards. This requires efficient tests in order to obtain information on the adsorption behaviour of the tested carbons for practical use.

As measurements of defined organics are not conclusive for our raw water in practice, summary parameters must be used for analytical checking. For many years the method of extinction measurements in the UV range has proved a good parameter for this because this method

- can be carried out easily and quickly
- provides exact results, and
- requires no specially trained laboratory personnel.

At the Düsseldorf waterworks (Stadtwerke Düsseldorf AG) such measurements are carried out in order to control the activated carbon filters.

The following numerical values are the result of these measurements:

- UV extinction of the filter inlet, E_o,
- UV extinction of the filter outlet, E, and
- throughput of water, V.

According to the formula

$$(1 - E/E_o) \cdot 100 = A$$

the values for E and E_o result in the actual adsorption efficiency, A, of the activated carbon filling in percentage for each time of sampling.

The specific throughput, V^*, in m^3 water/l activated carbon is calculated from the throughput of water, V, and the volume of the activated carbon, V_K in the filter according to the formula

$$V/V_K = V^*$$

The evaluation of many measurements showed that if the obtained values for the percent adsorption efficiency A are plotted against the specific throughput on a semi-logarithmic graph, the following empirical relation is found

$$A = A_o \exp(-kV^*)$$

in which the constants A_o represent the percent adsorption efficiency for a zero specific throughput, while k is the adsorption constant in $1/m^3$ (Table 1).

A_o and k can be taken from the diagram or, more precisely, can be determined by using a calculating programme using the corresponding pairs of values for A and V^*.

TABLE 1

a) Measurements

E_o	-	extinction of the filter inlet
E	-	extinction of the filter outlet
V	m^3	throughput of water
V_K	l	volume of the activated carbon

b) Evaluation

$$(1 - E/E_o) \cdot 100 = A$$

$$V/V_K = V^*$$

$$A = A_o \exp(-kV^*)$$

A_o	%	adsorptive power for V = 0
A	%	actual adsorptive power
V*	m^3/l	specific throughput of water (water/activated carbon)
k	l/m^3	adsorption constant
r	-	correlation coefficient
n	-	number of evaluated measurements

Using this relation, which was first found to apply to our large carbon filters, it is possible by the constants A_o and k

- to characterize the activated carbons
- to estimate filter running times, and
- to judge the reactivation effects

Of course, it was of interest in this connection to find out whether this relation is also valid for test filters of considerably smaller dimensions, and whether such results can be transferred to waterworks filters. If so, this would enable us to do test runs for our new or regenerated activated carbons in a comparatively short time.

In order to obtain conditions as constant as possible during this test, the test filters were fed with the untreated water of one pump works only, whereas the large filters got ozone-treated water from several pump works.

The conditions for the test concerning the large and the test filters are compiled in Table 2.

TABLE 2

formula sign			filters		factor f
			large	test	
filter surface	A_F	m^2	19,63	0,0154	1280
filter diameter	d_F	m	5	0,14	36
filter length	l_F	m	2,3	1,0	2,3
volume of the activated carbon	V_K	m^3	45	0,0154	2900
mass of the activated carbon	S_K	kg	18000	6,2	2900
discharge volume	$\dot{V}$	m^3/h	400-600	0,3	1650
filtration rate	v_F	m/h	20-30	20	1,3
time of direct contact	t	min	4,6-6,9	3,0	1,9
dissolved organic carbon	DOC	g/m^3	2,2	2,4	0,9
extinction (d=1m) (λ=240/254 nm)	E	-	6/2,5	10/5	0,5

Note: Commas are decimal points.

Figure 1 shows the experimental data and the calculated straight lines for an activated carbon "T" in a large filter (TG) and in a test filter (TV). This diagram clearly shows, for the large filter,

- a higher A_o value
- a more level course of the function, but also
- the larger dispersion of the measuring points due to the unsteady conditions of operation

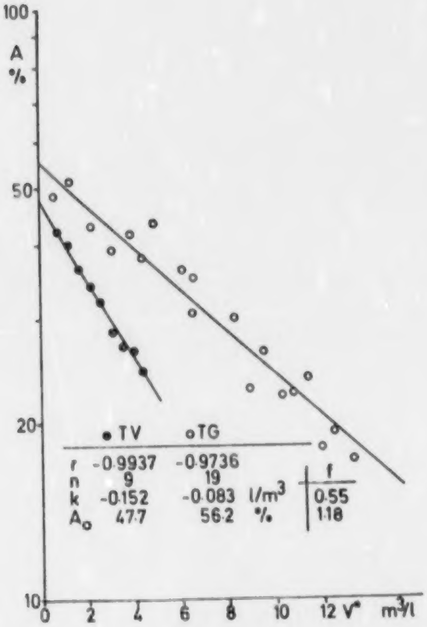


Fig. (1): Activated Carbon "T"

TV = test filter
TG = large filter

If one compares the constants for the large filters and the test filters, one finds that for the large filters

- the A_o values are higher by the factor 1.1 to 1.2 and
- the k values are lower by the factor 0.5 to 0.6

This means that, according to our experience, there are, by about the factor 2, higher loadings and longer filter running times, respectively, in large filters than there are in test filters.

It has not been possible so far to explain the reason for this different behaviour. It might be that the different geometrical conditions are responsible for this. Here, further studies will be made.

In order to show the influence of the wave length on which the UV measurements are carried out, the results for the activated carbon "T" are represented at $\lambda = 240$ nm and $\lambda = 254$ nm in Fig. 2. As a rule, a parallel shift with higher values for $\lambda = 254$ can be found, whereas k practically does not change. Presumably this effect can be attributed to the influence of the nitrate ion which adsorbs at 240 nm.

However, as
- the measurements provide more precise results on the average at 240
- the contents of nitrate are nearly constant and their changes do not affect the accuracy of the measurements, and as
- most of the experience has been gained on this wave length

this wave length is maintained for internal tests.

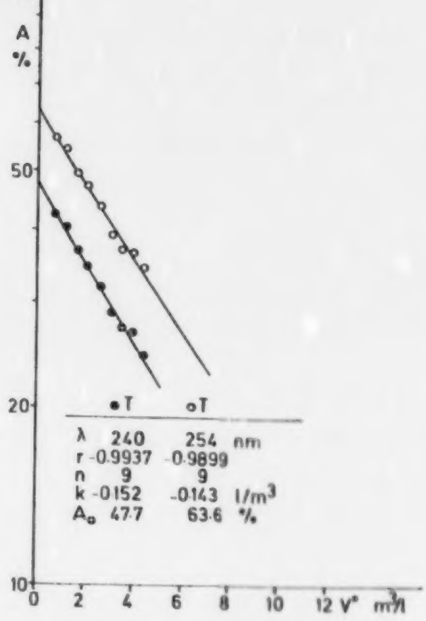


Fig. ([illegible]): **Activated Carbon "T"**

Measurements at 254 nm and 240 nm
(test filter)

Apart from a careful choice of new activated carbon, whereby many difficulties have been avoided by this test, the reactivation of loaded activated carbon is of eminent interest. This year a plant will be put into operation on site to reactivate the activated carbon used in 30 large filters with a total weight of about 500 t.

As shown by the reactivation tests carried out so far, this method permits to prove the influence of the parameters, temperature and time of direct contact, on the adsorption behaviour of the reactivated carbon during thermic reactivation. Thus we were in a position to adjust these conditions so that the quality of fresh coal was regained, or even surpassed occasionally, as can be seen in Figs. 3 and 4 showing fresh and reactivated carbons "F" (FF and FR) and "L" (LF and LR). These results of measurement were achieved in large filters.

On account of general experience we could assume that a reduction of the average grain diameter would lead to a higher adsorption efficiency. Two different activated carbons were examined in the test filter with two different medium-size grains in order to check this assumption.

Fig. 5 shows the results of a test with an activated carbon "S" with an average grain diameter of 1.2 mm (S12) and 2.0 mm, resp. (S20). Here the difference in capacity amounts to nearly 30 % within the scope of the measurements. This difference becomes even more evident in Fig. 6 where data for an activated carbon "C" with an average grain diameter of 1.0 (C 1L) and 1.8 mm (C 18) resp.are shown. Here the considerably increased values of adsorption at the beginning of the test are most striking, which are probably caused by a certain portion of fine carbon.

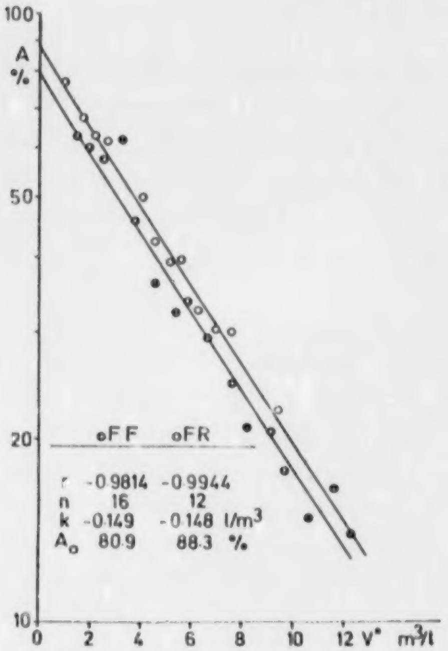


Fig. (3): Act.Carbon F"(large filter)

FF = fresh coal
FR = reactivate

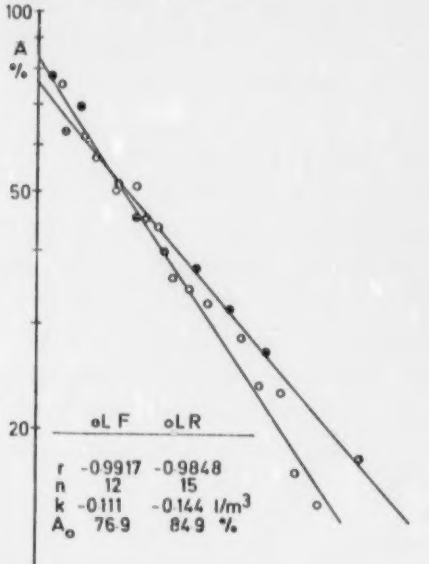


Fig. (4): Act.Carbon "L"(large filter)

LF = fresh coal
LR = reactivate

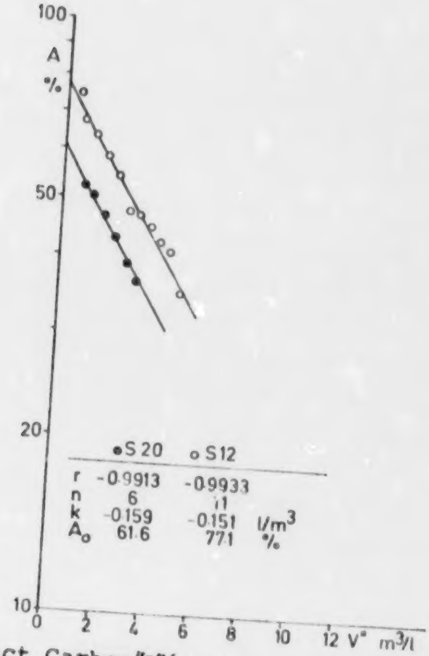


Fig. (5): Act.Carbon"S"(test filter)

S 12 = average grain diameter 1,2 mm
S 2o = " " " 2,o mm

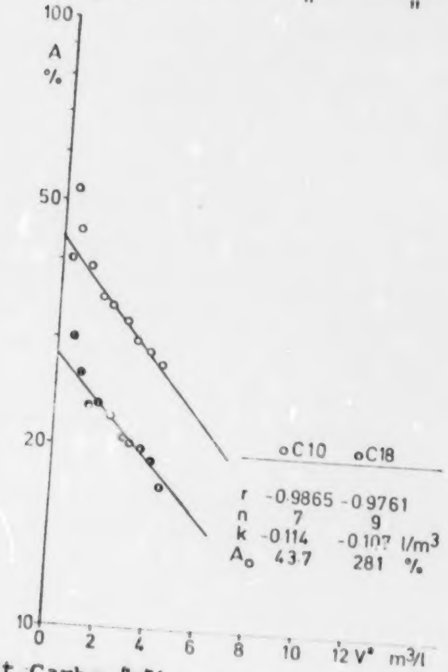


Fig. (6): Act.Carbon"C"(test filter)

C 1o = average grain diameter 1,o mm
C 18 = " " " 1,8 mm

The observed increase in adsorption efficiency with a decreasing average grain diameter, which was found in a test under conditions similar to practice encourages the use of activated carbon with as low a grain size as possible. However, there are certain limitations to the practical operation of fine granules because, on the one hand, there is the danger to lose them during backwashing, while, on the other hand, the increase of pressure will become to high during filtration. In this context, the question must be examined of how the grain distribution effects the reactivation.

Finally, two additional examples in Fig. 7 are to show how a comparatively small inner surface or an insufficiently developed supply pore volume take effect. The inner surface of the A coal "W" is at approx. 850 m^2/g at the lower limit of currently used activated carbons for water purification and shows, according to our standards, a totally insufficient adsorption efficiency. Although the inner surface of the A coal "H" amounts to 1,200 m^2/g, the adsorption capacity is also unsatisfactory here, which probably has to be attributed to the insufficient supply pore volume, particularly as the average grain diameter of 0.74 mm is at a very low level.

To summarize the results of this activated carbon test, the following conclusions may be made: The adsorptive power of activated carbons can be characterized under conditions similar to practice by the values A_o, the adsorption for the specific water throughput by zero, and k, the adsorption constant. These two constants allow a comparison of different activated carbons as well as predictions about the prospective running time of a filter. The results of the test filters, which are completed after a minimum of three and a maximum of eight days, can also be taken to predict the performance of large filters.

At present, an attempt is being made to find correlations between UV measurements and DOC or DOCl measurements by means of parallel investigations in order to obtain additional criteria of evaluation.

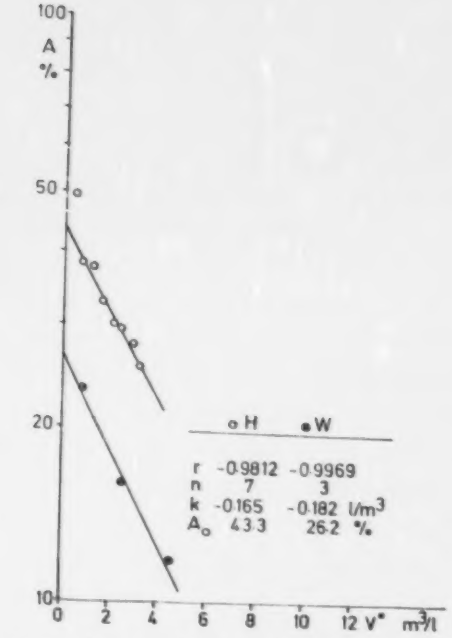


Fig. (7):Activated Carbons "H" and "W"
(test filter)

REALISTIC LABORATORY TEST METHODS FOR THE EVALUATION OF ACTIVATED CARBON

by H. Sontheimer

Experience to date indicates that the present test methods such as phenol value and iodine number for evaluating the characteristics of activated carbon give no useful information for drinking water treatment, because they make no valid statement on the effectiveness of different types of carbon in waterworks filters. This is the case not only when using activated carbon in water treatment. Thus, the use of molasses for testing activated carbon for decolourization of sugar solutions shows that test methods directly related to practical requirements are also of advantage in other industries (BRATZLER 1944, BAILLEUL 1962, HASSLER 1967).

As the common test methods cannot be transferred, better techniques had to be found, and some studies of more relevant methods have been published. In this connection the studies made by WEISSENHORN in Düsseldorf have produced an interesting method, requiring a pilot plant. However, the measurements need 8 to 14 days and do not allow a rapid evaluation.

Studies made at the Engler-Bunte-Institut, carried out in conjunction with different waterworks, were undertaken to develop a process for laboratory tests, taking as a guide for the results the data obtained from large filters, as they have been reported by FUCHS. The requirements for a laboratory test method to test activated carbons used in waterworks have been summarized in the following summary.

1) Realistic test conditions
   - a) low concentrations
   - b) similar organic substances as in the treated water

2) Orientation towards the practical problem
   - a) adsorption from a mixture
   - b) investigation of the specific effect for the adsorption of organo-chloro compounds and of the total amount of dissolved organics

3) Rapid and simple procedure
   - a) simple method of analysis (UV extinction)
   - b) orientating results with few measurements

4) Orientation towards the technical process
   - a) measurement of the adsorption equilibrium
   - b) measurement of the adsorption kinetics

The test conditions should be realistic, which makes it essential that the work is carried out in the same concentration range as is found in waterworks and also with similar organic compounds, as results can only then be expected which can be transferred to the behaviour of large filters.

The activated carbon filters have to meet different requirements simultaneously in the different works - in most cases the two problems of special importance are the removal of hazardous organo-chloro compounds and a certain reduction in the overall concentration of dissolved organics. Because different behaviours were observed with different types of carbon, particularly in respect of the above aims (FUCHS 1975), specific results ought to be obtained concerning the effectiveness in connection with these two tasks, while using a mixture of adsorptives. At the moment no statement can be made on the behaviour of a mixture from investigations with single substances only (FRITZ 1974, BALDAUF 1975).

Moreover, the test ought to be rapid and simple. This aspect is of particular importance for the control of regeneration plants such as are being installed in some works at the moment. This requirement excludes all complicated methods of analysis. However, certain mixtures of organics can be examined by UV measurements (JAFFEE 1962, FRITZ 1974) with two wave lengths in a very short time.

Upon thorough reflection, it became apparent that relevant results on the technical processing can only be rapidly obtained when equilibria and kinetics measurements are made simultaneously. However, combined measurements in a filter test have the disadvantage that they require too long a time.

From the onset, one of the main problems was to find a suitable mixture of substances. An exceptional number of tests were made in this connection, just one example of which is presented in this report (Fig. 1); further examples can be seen in the ARW reports (1972-1974).

Fig. 1: Simultaneous adsorption of tetrapropylene benzolsulfonate

Here a mixture of tetrapropylene benzolsulfonate (TBS) and chloro-phenol was used; both in a relatively high concentration. The residual concentrations and loadings are listed in the Figure. One can see that the order of the carbon adsorption capacity for TBS corresponds with that which is obtained in

Aktivkohle-sorte	TBS		p-Chlorphenol		Gesamt
	Restkonz in mg/l	Beldng mg/gAK	Restkonz in mg/l	Beldng mg/gAK	Beldng mg/gAK
F 300	28,7	142	29,3	138	280
Norit supra	28,5	143	27,5	150	293
Nuchar	29,6	136	27,5	157	293
BS	33,6	109	23,3	178	287
LSS	37,7	82	20,8	195	277

Fig. 1

Aktivkohlesorte: type of activated carbon
Restkonzentration: residual concentration
Beladung: loading
Gesamtbeladung: total loading

practice concerning the removal of the overall concentration of organics. One can also see that the order is the reverse concerning the removal of chlorophenol, which also corresponds to that which is observed in practice.

The use of the above, or a similar mixture of two defined organics,seems to be quite successful and should be investigated in greater detail. However, there are still a number of problems concerning the analytical methods and the choice of organic pairs.

The use of such a mixture has the major advantage that such a test can also be carried out by the manufacturer. Nevertheless, there is the disadvantage that this test will not take into account the different conditions existing at each waterworks, which have an effect on the optimum choice of carbon, as can also be seen from the results obtained from large filters.

We have therefore decided, especially with regard to controlling reactivation plants, first of all to develop a test using raw water which is to be treated with activated carbon. To this water p-nitrophenol (pNP) is added as a substitute for chloro compounds, because the latter cannot be easily measured by UV analysis. The behaviour of this substance towards adsorption is similar to that of the chloro compounds, and because it belongs to the important toxicological group of nitro compounds it is of some significance in practice too. The advantage of pNP is that it can be easily measured by UV analysis since it has a distinct peak at 317 nm. The exact method of procedure during this test is described below.

As a first step, the UV extinction of the raw water is measured at 254 nm and at 317 nm. When the specific UV extinction, i.e. the relation of UV extinction to the concentration of dissolved organic carbon (DOC), is known, the DOC can be calculated from these data. Instead of the raw water, a solution of a carbon extract can be used which should have about the same DOC. If the specific UV extinction is unknown, the DOC value should also be measured. Although this value does not vary greatly with time, it must be checked occasionally. It is possible too to use the UV extinction in m^{-1} (equivalent pathlength 1 meter) /as a concentration figure.

Nitrophenol is added to the test water in two different amounts (e.g. 0.8 mg/l and 4 mg/l). It is also possible to use one concentration only (2 mg/l) and run a parallel test using raw water alone. Then the activated carbon is added (20 mg/l and 40 mg/l) which has been finely ground in order to reduce the time required to achieve equilibrium. The degree of grinding influences the adsorption time (3-24 hours). The carbon is then filtered off and the UV extinction determined at 254 nm and at 317 nm. Prior to the measurement the sample must be acidified, otherwise errors may result in the UV measurements. From the UV data the DOC values can then be calculated.

Fig. 2: Summation of spectra of processed river bank filtrate from the Rhine and p-nitrophenol at equal DOC rates

Fig. 2 shows the superimposed curves of the two test substances. For a statement on the two concentrations two measurements are required which are in the region of the peak at 317 nm and of the minimum at 254 nm. For a calculation of the two unknown concentrations it is assumed that the UV extinction increases proportionally to the DOC, so that the specific UV extinction is necessary as an additional value for the calculation. In Fig. 2 the two formulas are shown which are required

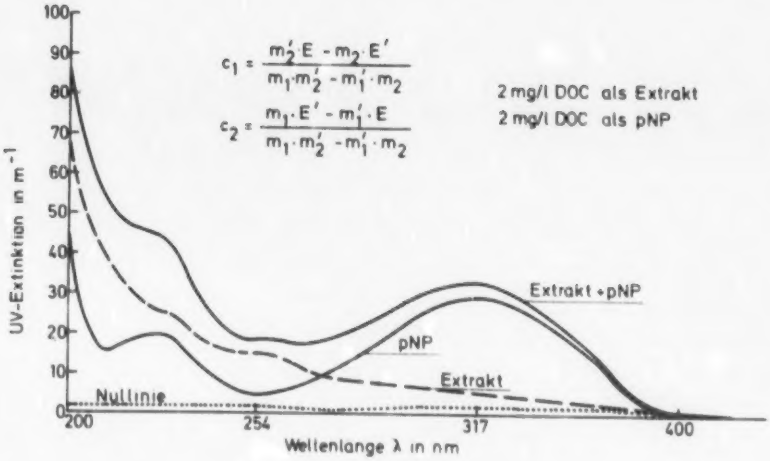


Fig. 2

Nullinie: zero line

Wellenlänge: wave length

2 mg/l DOC als Extrakt: 2 mg/l DOC as extract

for the calculation of the concentration of the original organic substances or the carbon extract (Ex), respectively, and those of p-nitrophenol (pNP). The symbols in Fig. 2 are set out below. -

c_1 = concentration Ex (mg DOC/l)
c_2 = concentration pNP(mg DOC/l)
E = UV extinction at 254 nm (m^{-1})
E' = UV extinction at 317 nm (m^{-1})
m_1 = spec. UV extinction of Ex at 254 nm
m_1' = spec. UV extinction of Ex at 317 nm
m_2 = spec. UV extinction of pNP at 254 nm
m_2' = spec. UV extinction of pNP at 317 nm

$$\text{spec. UV extinction} = \frac{\text{UV}}{\text{DOC}} \quad \left(\frac{m^2}{g}\right)$$

The simple relationship expressed in the two formulas is also valid for other substances.

As can be seen in Fig. 3, when there is a mixture of organics in the raw water or in an extract, their composition may change through adsorption.

Fig. 3: Change of UV-DOC dependence by adsprption onto activated carbon

Normally, any decrease of extinction should lead to a corresponding DOC decrease. However, this is usually smaller so that a correction may become necessary; one example is shown in Fig.3. One can easily determine experimentally the correction function, for example, from the knowledge of the outflow values of the

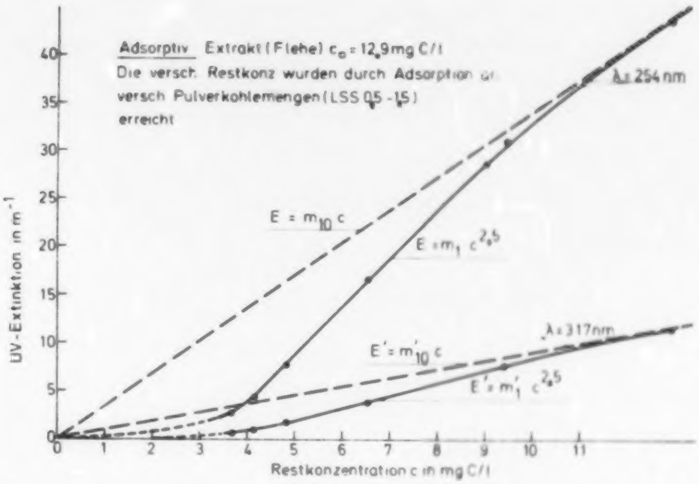


Fig. 3

Die versch. Restkonzentrationen... : The various residual concentrations were obtained by adsorption onto different amounts of powdered carbon.
Restkonzentration: residual concentration

carbon filter and from the change in specific UV extinction occurring through filtration. In cases where the following relationship, which can be seen in the figure, is valid for extract (Ex)

$$E = m_1 \cdot c_1^{2.5} = m_1 \cdot c_1^{n}$$

the calculation formula for c_1 shown in Fig. 2 must be modified as follows:

$$c_1 = \left(\frac{m_2' \cdot E - m_2 \cdot E'}{m_1 \cdot m_2' - m_1' \cdot m_2} \right)^{1/n}$$

The formula for c_2 remains unchanged since with pNP there is always a linear relationship between UV and DOC.

Through the described measurements and calculations all the data are obtained which are necessary for the test evaluation, typical results of which are shown in the following Table.

Table 1: Results of comparative tests of activated carbon with bank filtrate Flehe

AK	Zugabe an		UV-Extinktion bei		DOC für		% Entfernung		AK-Verbr. für eine Entf.	
	pNP g/m³	AK g/m³	254 nm m⁻¹	317 nm m⁻¹	org.Sub. g/m³	pNP g/m³	org.Sub. %	pNP %	org.Sub. 50 %	pNP 90 %
Lsg 0	0	0	5,08	1,95	2,0	0	-	-	-	-
Lsg A	0,8	0	5,60	7,46	2,0	0,414	-	-	-	-
Lsg B	4,0	0	8,02	29,58	2,0	2,07	-	-	-	-
AK M	0,8	20	1,16	0,52	1,10	0,006	45	98,6	27,6	8,8
	0,8	40	0,66	0,22	0,89	0,001	55	99,8	27,6	8,8
	4,0	20	2,90	10,92	1,32	0,77	34	63	49	35
	4,0	40	1,24	2,0	1,07	0,12	46	94	49	35
AK L	0,8	20	2,44	0,98	1,49	0,003	25	99,3	48,2	3,5
	0,8	40	1,20	0,42	1,12	0,001	44	99,8	48,2	3,5
	4,0	20	3,84	11,62	1,56	0,79	22	62	63	36,8
	4,0	40	1,8	2,62	1,26	0,15	37	93	63	36,8

$m_1 = 0{,}898$ $m_1' = 0{,}345$

$m_2 = 1{,}420$ $m_2' = 13{,}35$

Note: Commas are decmil points

Table 1

Zugabe an: addition of

UV Extinktion bei: UV extinction at

%Entfernung: removal in percentage

AK-Verbrauch...: consumption of activated carbon for the removal of organics

AK: activated carbon

In the uppermost line the data of the raw waters are listed, and below the data of the waters to which p-nitrophenol has been added. The increase of the extinction at 317 nm after the addition of p-nitrophenol is particularly noticeable. The two solutions were then mixed with 20 mg/l and 40 mg/l of activated carbon. Two different types of carbon were used in this test. After the equilibrium was achieved the UV values were measured again. They indicate that both carbon types have slightly different properties. Lower values were obtained with carbon type M for both wave lengths, so this carbon has better qualities in this case.

This can be seen even more clearly from the DOC values which were calculated from the extinctions, according to the formulas given previously. They also show that a conversion was necessary because the differences between the two types of carbon are only evident when the total amount of organics is compared, whilst the effectiveness with p-nitrophenol is similar, within the range of error. The smaller dosage of pNP was nearly completely adsorbed in both cases, so that in fact smaller amounts of carbon would have been sufficient in these experiments.

The simplest way of evaluating these data seems to be the calculation of the percentage of removal. More informative, because it can be converted directly into operation costs, is to determine the consumption of activated carbon required for a definite degree of removal of the two groups of substances. For this purpose it has to be assumed that the adsorption kinetics can be described according to FREUNDLICH.

If we define: c_0 = initial concentration (g/m^3)

c_1 = concentration after addition of A_1 of activated carbon (g/m^3)

c_2 = concentration after addition of A_2 of activated carbon (g/m^3)

$$Q_1 = \frac{c_0 - c_1}{A_1} \qquad Q_2 = \frac{c_0 - c_2}{A_2}$$

Using these figures, we can find the amount of activated carbon (g/m^3) which reduces the concentration by x per cent:

$$A = (c_0 - c^x) \cdot \exp_{10}(-F)$$

$$c^x = c_0 \left(\frac{100 - x}{100}\right)$$

$$F = \frac{\log c^x (\log Q_2 - \log Q_1) + \log Q_1 \cdot \log c_2 + \log Q_2 \cdot \log c_1}{\log c_2 - \log c_1}$$

Making use of a simple calculation procedure, A can then be calculated for different values of x. In Table 2 the values are given for 50 per cent removal of extract and 90 per cent removal of pNP.

These results show that, in the presence of large amounts of p-nitrophenol, which has a suppressing effect, the adsorption performance for the total amount of organics declines considerably. This results in an increased carbon demand of about 30 to 70 per cent. The difference in efficiency of the two types of carbon is also visible from the data in Table 1.

The extent to which different types of organics can influence their possible removal by adsorption is shown in Table 2.

Table 2: Comparative tests using different extracts with the same carbon quality

Extraktherkunft	p-Nitrophenolzug		Kohleverbrauch bei den Sorten N und L			
	in g/m^3	DOC$_o$ Extrakt in g/m^3	50%.Entf org Subst	90%.Entf pNP	50% org Subst	90% pNP
Koln	0,8	2,04	26	19	33	10
Koln	4,0	2,04	51	46	50	40
Holthausen	0,8	2,60	42	18	44	1
Holthausen	4,0	2,60	62	47	74	38
Langenau	0,8	1,58	21	21	31	4
Langenau	4,0	1,58	36	50	41	41

Table 2

Extraktherkunft: origin of extract

p-Nitrophenolzugabe: addition of p-nitrophenol

Kohleverbrauch... : consumpt. of carbon type N and L

50% Entf.: 50 per cent removal

The Table gives values for three extracts on two carbon types. From the data it can be seen that the DOC decrease and the carbon consumption, designed to achieve a defined effect, is different with each type of water, and that the carbon types react differently too. This justifies the use of raw water for the test because the given results conform with the practical experience gained with large filters.

The most expressive and perhaps the most useful way of evaluation of the analytical data is shown in Fig. 4.

Fig. 4: Dependence of the purification effectiveness of an activated carbon filter on the water throughput for each m^3 of activated carbon (or on the running time of the filter)

Plotted here is the percentage elimination as a function of the water throughput, which is proportional to the filter running time, at complete utilization of the carbon. The values can be calculated from the carbon consumptions required for a defined degree of removal. For this it is merely necessary to know the bulk weight and to estimate the height of the layers and the filter velocity in a filter. In this example, a height of 2.5 m was assumed for the carbon layer and a filter velocity of 15 m/h. Plotted are the values for the residual concentration of the overall DOC and the p-nitrophenol after certain filter running times, in each case in relation to the initial concentration. Here again, the analytical data of the tests with two different carbon types, shown in Table 1, are used to illustrate the significance of the results. From the position of the curves the advantages of the carbon type L for both parameters can be seen; however, after a certain running time the curves for the extract overlap. In general, there are no great differences, they amount to 10 per cent in

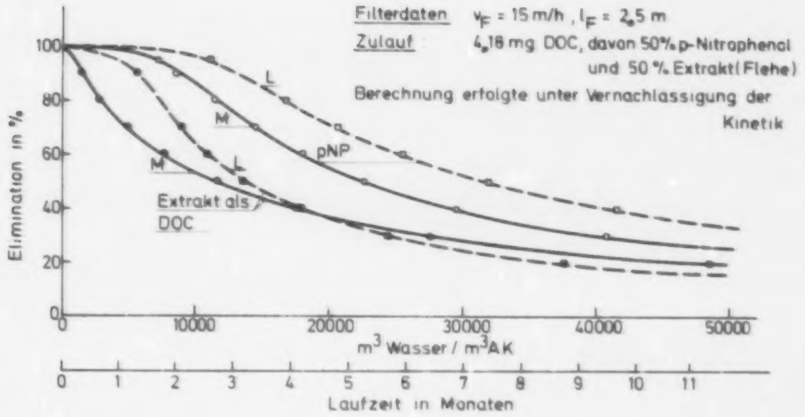


Fig. 4

Filterdaten: filter data

Zulauf: feed

Berechnung...: calculation was made **without kinetics**

Laufzeit in Monaten: running time in months
4.18 mg DOC, davon...: 4.18 mg DOC, of which...

m^3 Wasser/m^2 AK: m^3 water/m^3 AC

Extrakt als DOC: Extract as DOC

this particular case, at an average running time of three months. If the difference in price for both carbon types were to be of this order, related to the costs for one filter filling, then both types of carbon would be equal.

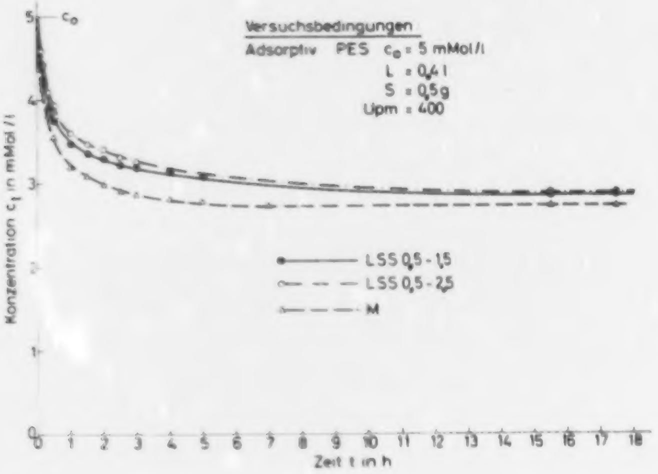
However, the above is only valid when there are no additional rating criteria, i.e. if it were possible to describe the behaviour of activated carbon filters solely by equilibrium measurements. This is not so, in fact kinetic measurements are required as well. That this is of importance as regards the two carbon types in question has been made clear by a parallel filter test made in Düsseldorf, which showed a greater difference between the two carbon types than had been calculated from the equilibria measurements. Therefore, kinetic measurements were also made, using first phenyl acetic acid (PAA) at high concentrations, the results of which are shown in Fig. 5.

Fig. 5: Adsorption kinetics with different types of activated carbon with phenyl acetic acid

The illustration shows the progress with time for the adsorption process using three different types of carbon. The amounts used were measured by weight, not by volume, which is of importance in this case because of the very much lower bulk weight of carbon type M. It may be seen that the equilibrium concentration using carbon type M is slightly better under the test conditions, and that this type shows a more favourable kinetic behaviour under the high concentrations used in this test.

This relation between the different types of carbon did not change when, instead of PAA, an extract was used which had about the same concentration.

Fig. 6: Adsorption kinetics on different types of carbon with extract (Flehe)



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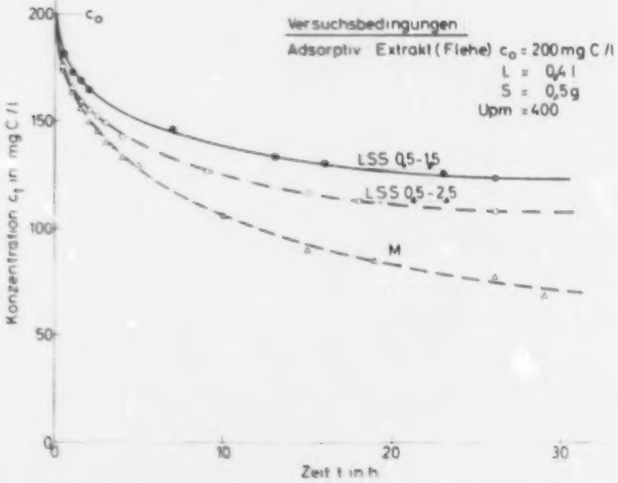


Figs. 5, 6

Versuchsbedingungen: test conditions
UpM: rpm
Zeit t in h: time t in h
PES: Phenyl acetic acid
Konzentration: Concentration

However, under the chosen test conditions, i.e. equal carbon dosage in mg/g, the residual concentrations differ considerably so that it is difficult to draw any definite conclusions.

Special calculation proves too that at the high concentrations of dissolved organics there is no obvious difference between the three carbon types concerning the adsorption kinetics, but they differ regarding equilibria data.

However, this situation changes when the adsorption kinetics are investigated in the region of low concentrations (see Fig. 7).

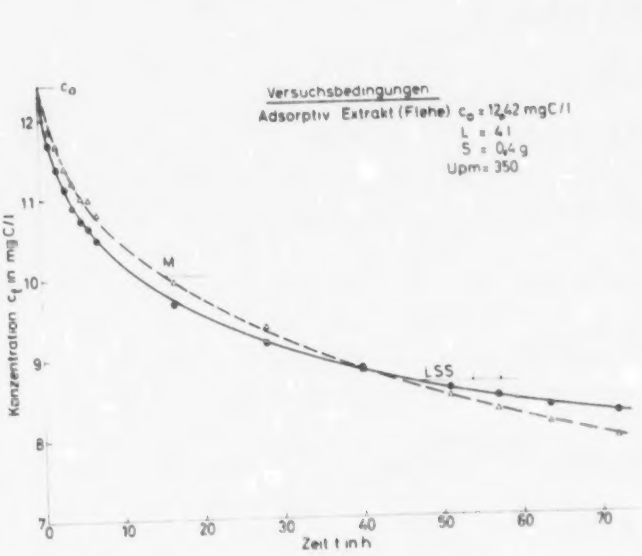
Fig. 7: Adsorption kinetics using equal amounts of different types of carbon

Here not only the adsorption equilibria are very similar - contrary to the behaviour at high concentrations - but it is also obvious that the carbon type M, which had the better adsorption kinetics at high concentrations, initially adsorbs less rapidly at the low concentrations than the carbon LSS. This example shows once more the importance of carrying out all test procedures in a realistic investigation of carbon properties in a range of concentration comparable with the actual conditions.

In this particular case, the differences illustrated in the figure explain the observations made in practice when taking into consideration the different bulk weight of the carbons.

If a test is made with carbon amounts of equal volume, the difference between the carbon types is still more evident, as can be seen from Fig. 8.

Fig. 8: Adsorption kinetics using equal-volume amounts of different types of carbon



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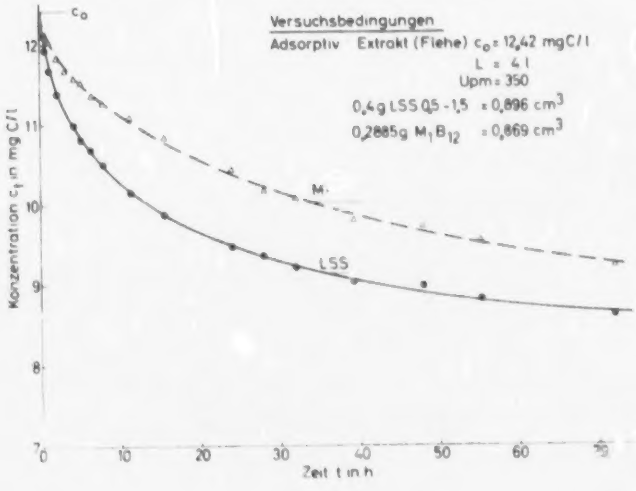

Abb.8

Figs. 7, 8

Versuchsbedingungen: test conditions
UpM: rpm
Zeit t in h: time t in h

Konzentration: Concentration

When the kinetic measurements, as shown in this figure, are taken together with the measured equilibria data, the conclusions obtained conform well with experience gained in practice and with effects observed in waterworks filters.

Nevertheless, extensive research and investigations are still necessary to be able to optimize the described test. For this purpose, appropriate samples should be examined at the waterworks which use activated carbon filters in the way as described above. If, parallel with such tests, the usual analytical measurements are made with the large filters, it should become obvious in the course of time how to evaluate the results from such tests in order to achieve concrete statements for practical use and thus obtain a clear criterium for activated carbon quality.

It will, furthermore, be necessary to extend the test procedure by using defined organic substances. This is essential to enable manufacturers of activated carbon to make a regular quality check and also to have a test method which is independent of fluctuations in the quality of the raw water. The choice of the defined individual substances should be determined by a comparison with the results obtained from tests with raw waters.

In conclusion it must be mentioned that the test methods for the evaluation of the quality of activated carbon discussed in this paper still have various shortcomings and are by no means ideal in every sense. There is still much work to be done in this field. The results obtained so far indicate, however, that the proposed procedure was a step in the right direction and that it is worth-while to continue the work in the manner suggested.

PHENOMENA OF ACTIVATED-CARBON REGENERATION

by

H. Jüntgen, Essen

Introduction

The adsorption of organic matter by means of activated carbon in a filter is a known nonsteady process, i.e. after a period of time determined by stream rate, concentration of the matter to be adsorbed and by the adsorption capacity of the activated carbon, the filter has reached the limit of its capacity so that no further adsorption can take place. The spent activated carbon has to be regenerated then. The term "regeneration" stands for the removal of the adsorbate and simultaneous re-establishment of the previous adsorption capacity of the virgin activated carbon. The regeneration of spent carbon used in water works may be carried out basically by means of extraction or by thermal treatment. The present paper shall be confined to the last-mentioned treatment.

The thermal regeneration is carried out in two steps: at temperatures above approx. 100 °C desorption of the water and of most of the organic matter adsorbed is started. As will be explained later on, it is impossible, however, to obtain complete desorption of all adsorbate so that in a second step a reactivation of the activated carbon must be carried out in order to destroy the residual load remaining after desorption, and to re-establish the former adsorption capacity of the activated carbon. Generally, for this purpose a reaction by means of oxidation agents under well defined conditions is used.

2. Desorption mechanism

The desorption of adsorbates from activated carbon has been studied in detail. It is known that desorption is a first-order reaction. Its rate is proportional to the residual load at a time t. (HAYWARD, 1964). The activation energy of desorption in that case must be greater or equal to the adsorption energy. In order to avoid back-reaction (in our case this means adsorption), the adsorbate must be removed from the surface as soon as possible. This can be carried out e.g. by use of a flushing gas.

Bergbau-Forschung developed a non-isothermal measuring method to study the desorption of adsorbates from activated carbon.[2] A set up using that method is shown in Figure 1. The sample is placed on a wire mesh through which a pre-determined quantity of flushing gas is led. By means of an electric heater the wire mesh and the sample are heated up at constantly increasing temperature. Simultaneously, the adsorbate is measured (by a downstream gas chromatograph or a mass spectrometer) versus time or versus sample temperature. Figure 2 shows a typical result obtained by this technique. The quantity per time unit of phenol desorbed by activated carbon is plotted as a function of sample temperature. During these tests a constant heating rate of 2 °C/min. was maintained. It may be seen that desorption at low stream rate of the flushing gas is slow and does not reach its end but at temperatures of approx. 4oo °C, i.e. after 2oo minutes. If the stream rate is boosted to approx. 18 l/h, the end of desorption is reached at approx. 26o °C, i.e. after 13o minutes. By further increase of the flushing gas rate no reduction of the desorption time is obtained. In this way, the conditions under which a back-reaction is avoided have been found out. It is remarkable that desorption rate first increases rapidly, reaches a maximum and then decreases slowly. This phenomenon may be explained theoretically; however, when using the simple theory, another desorption curve, as shown in Figure 3, should be obtained. The curve calculated theoretically according to simple conditions presumed shows a less steep initial gradient and falls rapidly after having reached the peak. Detailed investigations have shown that the reason for this deviation from the simple theory is to be found in the desorption rate depending on the initial load, as shown in Figure 4. It may be seen that with low load, e.g. approx. 1 mmol/g, the maximum of desorption rate

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[2] (JÜNTGEN, VAN HEEK, 1970)

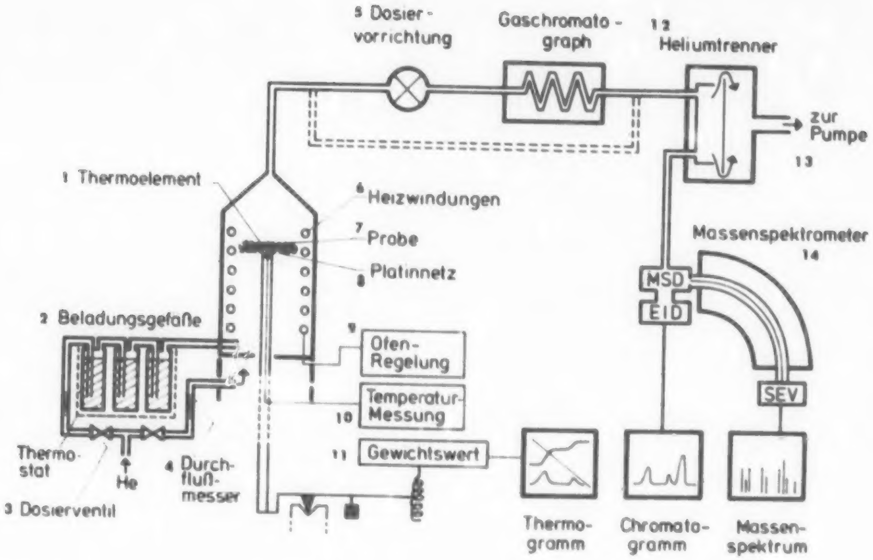
5 Dosiervorrichtung
Gaschromatograph
12 Heliumtrenner
zur Pumpe
13
1 Thermoelement
6 Heizwindungen
7 Probe
8 Platinnetz
Massenspektrometer 14
MSD
EID
2 Beladungsgefäße
9 Ofen-Regelung
10 Temperatur-Messung
SEV
Thermostat
He
4 Durchflußmesser
11 Gewichtswert
3 Dosierventil
Thermogramm
Chromatogramm
Massenspektrum

Fig. 1 Flow gas apparatus for the investigation of vapour desorption from activated carbon

1 Thermoelement: thermo-element
2 Beladungsgefäße: loading vessels
3 Dosierventil: dosage vent
4 Durchflußmesser: flow-through meter
5 Dosiervorrichtung: dosing unit
6 Heizwindungen: heating thermocouple
7 Probe: sample
8 Platinnetz: platinium net
9 Ofen-Regelung: furnace adjustment
10 Temperaturmessung: temperature survey
11 Gewichtswert: weight
12 Heliumtrenner: helium separator
13 zur Pumpe: to the pump
14 Massenspektrometer: mass spectrometer

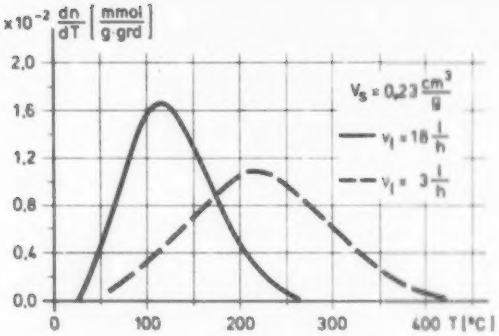

Fig. 2 Effect of flow rate on the desorption curve of phenol

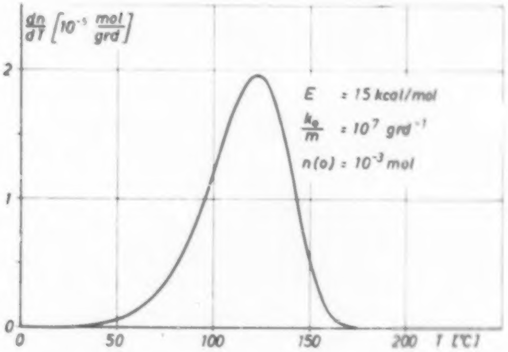

Fig. 3 Desorption curve calculated under simplified conditions

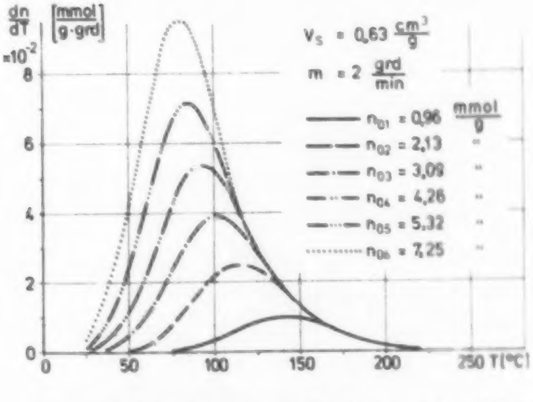

Fig. 4 Non-isothermal desorption of phenol from activated carbon at different initial loads

grd: ° Celsius

is reached at 15o °C. In this case, nearly a symmetrical curve is obtained. At high loads (7 mmol/g), however, the maximum is reached at 8o °C, but the curve then shows a tailing up to 22o °C. This behaviour may be explained by the binding energy between the adsorbate and the surface being dependent on the state of load. In case of an energetically heterogeneous activated-carbon surface centers with high adsorption heat are occupied first by initial small loads and then during further adsorption, centers of lower adsorption heat are occupied. The course of desorption is analogous: With decreasing residual load, activation energy of desorption increases.

Meanwhile, a theory has been developed which allows for the heterogeneity of the surface, so that actual curves of desorption can be established with sufficient precision. In many cases it is even possible to draw conclusions with respect to activation energy of desorption from the adsorption heat values calculated from one of the measured isotherms, both values being functions of the load. Thus, in case of a known isotherm, the course of desorption may be generally calculated in advance.[3] Figure 5 shows, for activated carbon of different micropore volumes, a comparison between the activation heat values (dotted line) measured during desorption of phenol, and the corresponding adsorption heat values measured during adsorption as a function of the load. It may be seen that in case of large-pore activated carbon (V_2 = o.81 g/cm^3) the respective data are fairly congruous, whereas with narrow-pore activated carbon (V_s = o.34 g/cm^3) the activation energies found for desorption are lower than the adsorption heat values found by adsorption measurements. The last-mentioned deviation may be explained as follows: Due to the high residual load at desorption in this particular case, the surface does not participate in its totality in the desorption, and especially the adsorption centers of higher activity do not desorb the bound adsorbate.

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3) (SEEWALD, 1974)

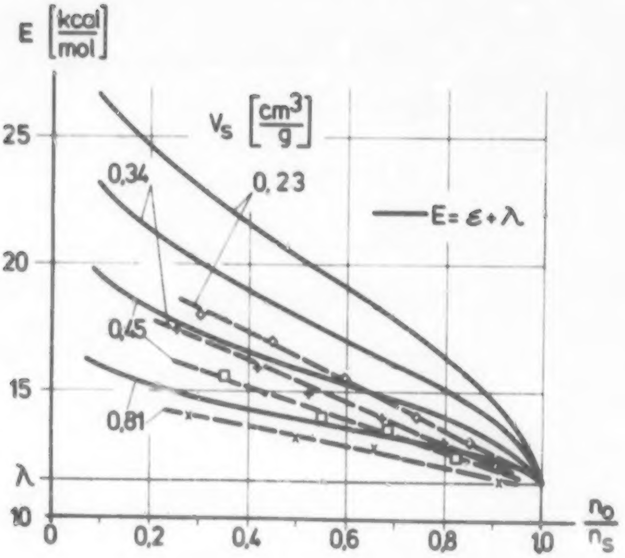

Fig. 5 Calculated and measured activation energies of phenol desorption as a function of amount adsorbed.

Thus, by supposing a first-order reaction for the desorption, and furthermore by means of the interdependence found between adsorption heat and the desorption's activation energy we obtain a satisfactory explanation and description of the desorption. This implies higher activation energy at desorption of substances which have been adsorbed more strongly, i.e. these substances are desorbed under analogous conditions in higher temperature ranges. An example is given in Figure 6 showing in the lower section a comparative desorption of phenol, cresol and naphthalene This comparison leads to the conclusion that in any case the molecule with a higher molecular weight and, thus, with a higher adsorption heat is desorbed at higher temperatures. From this, we further may deduce that the residual load increases with increasing adsorption heat and that substances with high molecular weight exist which are desorbed at such a high temperature that their decomposition takes place before the theoretical desorption temperature is reached. Normally, this phenomenon takes place simultaneously with the formation of carbon deposits on the surface. Furthermore, catalytic reactions of the adsorbate during thermal treatment, enabling dimerisation, polymerisation or condensation of the adsorbate, seem possible. Observations of that kind are observed e.g. in the case of phenol. The resulting residual load prevents the active centers of the activated carbon from being free after desorption, so that theoretically the initial activity of the activated carbon cannot be re-established. An example is shown in Figure 7, illustrating the adsorption capacity of different types of activated carbon after a series of desorptions (3oo minutes at 8oo °C). The activated carbon was charged with phenol.

All thus treated carbons exhibit considerable decrease in activity, possibly continuing until complete loss of the intial properties. For re-use of activated carbon loaded in this way, a re-activation seems appropriate.

Re-activation mechanism

Numerous investigations during production of activated carbon have shown that at increased temperature steam and other fluids react selectively with activated carbon in a way that the

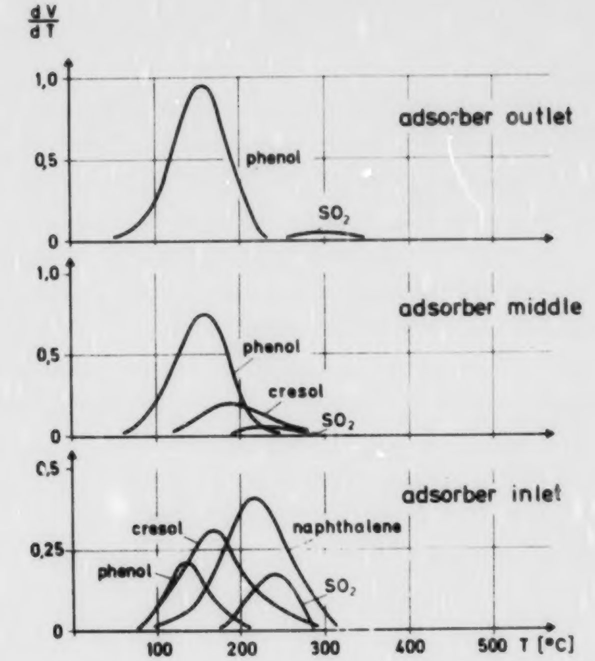

Fig. 6 Desorption of various compounds from activated carbon treated with waste water from a coke oven plant

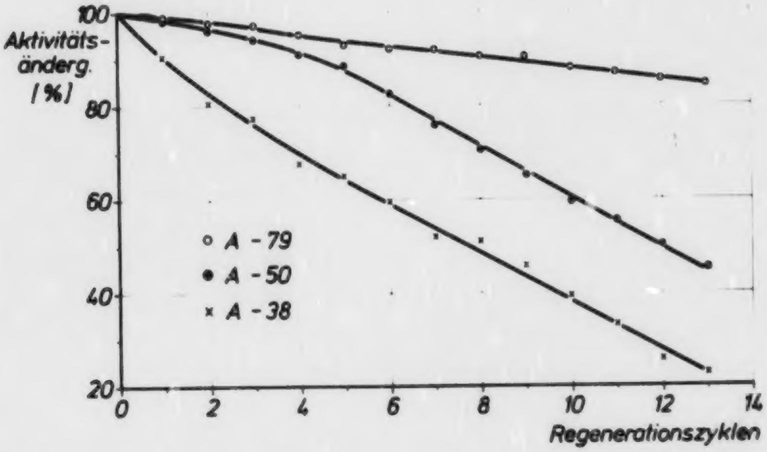

Fig. 7 Change of Adsorption capacity of different activated carbons as a function of phenol adsorption and desorption runs

Aktivitätsänderung : change in activity
Regenerationszyklen: regeneration cycle

reaction takes place immediately on the inner surface of the activated carbon. For this it is necessary that a temperature range is chosen in which the chemical reaction exclusively controls the rate for the whole course of reaction. Furthermore, it was found that the reactivity of the carbon surface is locally different. Faults in the grid structure or small crystallites with many edges react better than crystallites with larger surfaces. This might lead to the assumption that those carbonaceous compounds formed in the course of the thermal desorption treatment show a higher reactivity, due to their faulty structure, than the surface of the activated carbon. As a prerequisite, however, the activated carbon itself must have a relatively homogeneous carbon surface so that its reactivity is low from the beginning. Under these conditions it should be possible to treat the loaded activated carbon e.g. by a careful control of the water-gas reaction selectively, in a way that the remaining adsorbed matter is purposely destroyed in order to reestablish the previous surface structure of the activated carbon. In this field, detailed investigations have been carried out by Bergbau-Forschung. In the first place, these investigations dealt with the reactivity of virgin carbon. A typical result of these initial investigations is shown in Figure 8 illustrating the reactivity of different activated carbon qualities as a function of temperature.[4] The term "reactivity" stands for carbon matter gasified per unit of time by the water-gas reaction. These tests were carried out under constant partial pressure of steam. As expected, for all activated carbon qualities tested the reaction rate of steam decomposition rose exponentially with increasing temperature. It was surprising that the individual activated carbon qualities exhibit substantially different reactivity, and that obviously the raw material is a certain determining factor for these properties. The reactivity of activated carbon made from wood is particularly high compared with the low reactivity of activated carbon made from hard coal.

Figure 9 shows the curve of the reaction rate of a loaded activated carbon at different constant temperatures as a function of

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4) (REICHENBERGER, 1974)

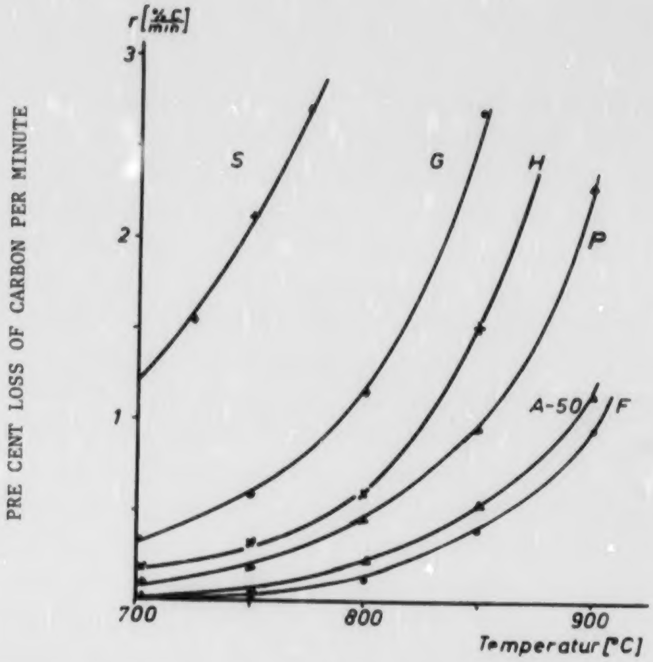

Fig. 8 Reactivity of activated carbon produced from different materials as a function of temperature

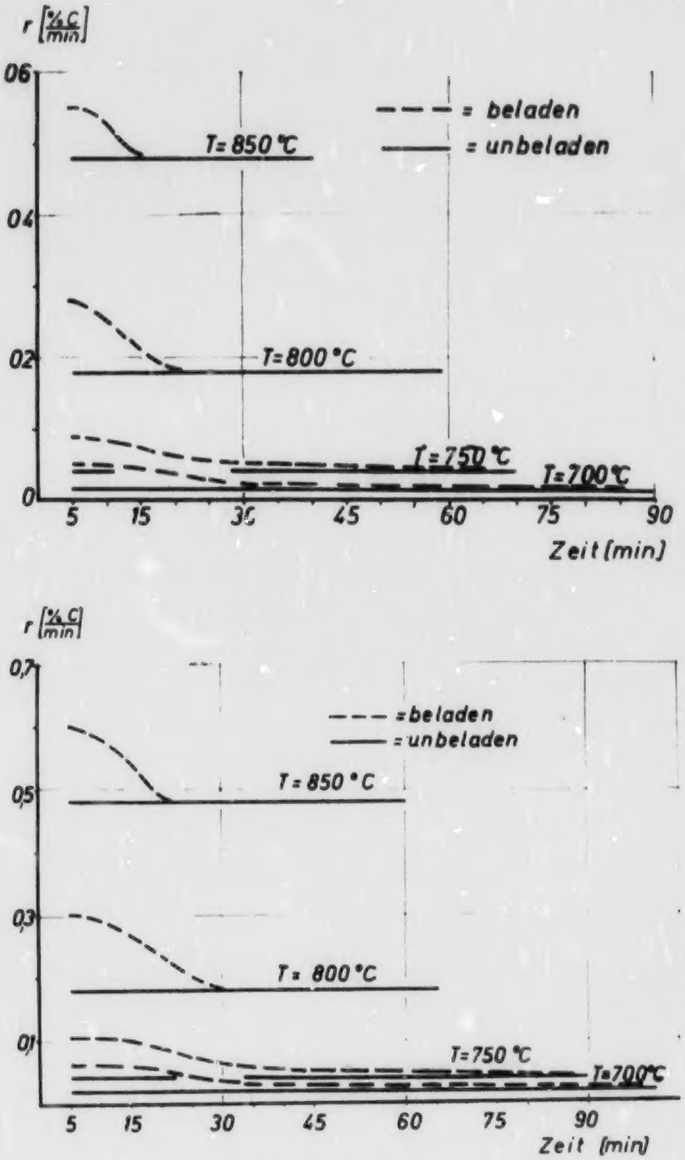

Fig. 9 Reactivity of untreated activated carbon in comparison to reactivity of carbon loaded with phenol (upper part) and components of waste water from a coke oven plant (lower part)

beladen: loaded
unbeladen: unloaded
Zeit: time

time. The upper part pertains to activated carbon loaded with phenol, and the lower part pertains to activated carbon used for treatment of coke oven plant waste water. A common feature of all curves is the fact that the loaded activated carbon initially shows a higher activity than the fresh activated carbon. After a characteristic period of time the initial reactivity decreases and reaches the values of non-loaded activated carbon. It is to be seen that the decrease to the reactivity values of untreated activated carbon is accelerated with higher reactivation temperature. According to the previous considerations, this phenomenon may be explained in that the water-gas reaction actually destroys first the carbon contained in the load. Further investigations have shown that the activity of regenerated carbon actually reaches its original value if reactivation is stopped at the specific point of time at which the reactivity has reached the value of fresh activated carbon. From figure 1o it may be seen that by reactivation of phenol-loaded activated carbon at a period of stay of 2o minutes at 8oo °C actually, even after many subsequent reactivations, a state of unchanged activity (upper section) and weight (lower section) is maintained. These reactivation conditions result from reactivity investigations. It is left up to the engineer to determine the reaction conditions for each specific case by appropriate choice of temperature and period of stay for the solid matter.[5] Of course, these reaction conditions depend to a very large extent on the kind and quantity of the adsorbate, as well as on the quality of the activated carbon used. By appropriate preliminary tests, however, it is generally possible to determine the conditions of desorption and reactivation enabling best-possible re-establishment of activity and very low losses of activated carbon during treatment. Losses of activated carbon occur always if reactivation is not carried out as selectively as described here. In such cases, the achievement of activity implies overactivation, i.e. a part of the activated carbon adsorbent is destroyed during reactivation.

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5) (JÜNTGEN, KLEIN, 1974)

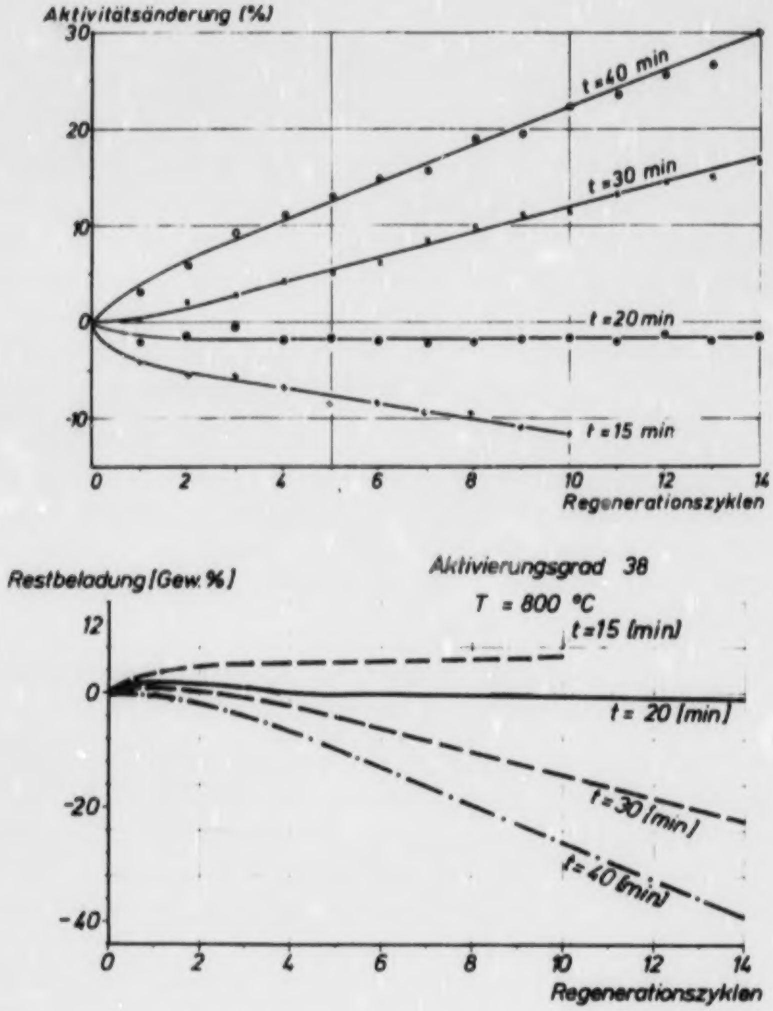

Fig. 10 Effect of residence time on activity and change of weight of activated carbon

Aktivitätsänderung: change in activity

Regenerationszyklen: regeneration cycle

Aktivierungsgrad: degree of activation

Restbeladung: residual loading

GEW %: % by weight

Aktivierungsgrad 38: Activation grade 38

Regeneration process

In practice, usually desorption and subsequent reactivation can be carried out in one process unit which, however, should be designed in a way to allow for appropriate sequence of operation steps. In special cases, two-stage operation is recommendable, i.e. if the adsorbates are to be recovered during desorption. In the past, generally rotary kilns were used for regeneration. In recent years, fluidized-bed regeneration has been practised to an ever-increasing extent. Fluidized-bed regeneration offers the following advantages:

1. Due to favourable heat and material transfer, the reaction is faster, so that smaller reaction volumes are required and the process takes less time. Thus, the reaction space of the fluidized bed can be kept considerably smaller than the one of rotary kilns.
2. The particles are in suspension during reaction. Thus, abrasion losses are smaller than with rotary kilns.
3. On the basis of sufficient knowledge and by means of appropriate techniques, the retention time distribution for the solid matter in a continuously operated fluidized bed may be controlled, i.e. the required average period of stay can be reliably adjusted and rapidly re-adjusted or adapted, if necessary, according to the operational requirements.
4. By a reactor design it is possible to impose strict limits to the retention time distribution so that a homogeneously reactivated product is obtained and, at the same time, the losses during reactivation are minimized.

However, design and construction of a fluidized-bed reactor require considerably more information than the construction of a rotary kiln.

Conclusions

It has been shown that regeneration comprises two steps, i.e. desorption and reactivation; both have been investigated as to the phenomena involved, and can now be controlled operationally. In normal practice, one single process unit comprising different zones is used. At present, the use of a fluidized bed for reactivation is to be regarded as the best technique.

OPERATION, PROBLEMS, AND ECONOMY OF ACTIVATED CARBON REGENERATION

by B. Strack, Wuppertal

Introduction

The use of activated carbon in industrial processes for the adsorption of organics from liquids and gases has been known for centuries. In the waterworks of the Lower Rhine activated carbon has been used for water treatment since the 1960s and is becoming of increasing importance.

The constantly increasing problems of water treatment and thus the increasing use of treatment material and chemicals forced the waterworks to give further considerations to the use and to the economical regeneration of suitable activated carbon.

As the problems in the different waterworks of the ARW (Arbeitsgemeinschaft Rheinwasserwerke) were of a similar nature, an intensive exchange of experience has been taking place in recent years.

Outstanding support was given in this connection by the Water Chemistry Section of the Engler-Bunte-Institute at Karlsruhe, the Mining Research Institute at Essen, together with the manufacturers and suppliers of activated carbon and constructors of the relevant processing plants.

Present processing techniques

At present, activated carbon is bought from and regenerated by the manufacturers situated in Germany and abroad. The regeneration requires an exact schedule planning and agreement between the waterworks, the transport firms and the activated carbon manufacturers.

Any interruptions which may be caused by one of the firms taking part may lead to a disruption in the processing sequence. This makes it essential to maintain appropriate capacity for storing exhausted, regenerated, and virgin carbon. Also, there must be facilities for the removal of carbon and the filling of the filters. The same applies to the loading and unloading of the carbon transporters.

Apart from considerations of economics, the technical requirements led to the conclusion to include the regeneration furnace in the waterworks in the carbon cycle between the filter, storage containers and the transportation facilities.

As the additional facilities would require further space and would also incur higher costs than the actual reactor, and as these facilities would have to be adjusted to meet the requirements of each waterworks, the planning and tests described here for the Benrath waterworks of the city of Wuppertal are to be regarded as an example. Therefore, a description of this waterworks is given below.

Layout and operation of the Benrath waterworks

The waterworks is divided into 6 main sections:

raw water tank, 6000 m^3 capacity
plant house
filter plant, consisting of 16 filters
pure water tank, 10000 m^3 capacity
sedimentation tanks and sludge treatment facilities
auxilliary buildings

The positioning of the individual sections of the waterworks is dependent on the process requirements. A layout of the works is shown in Fig. 1

Fig. 1: Ground plan of Benrath waterworks

The Rhine bank filtrate is lacking in oxygen and contains small quantities of iron, manganese and ammonium ions. It contains excessive aggressive carbon dioxide and is heavily loaded with organic odour and taste substances. Based on pilot plant tests, a treatment process was chosen with the following process steps:

Open Spraying Tower - Ozone Contact Filtration - Activated Carbon Filtration

Fig. 2: Schematic layout of the Benrath water treatment plant

During spraying the raw water is saturated with oxygen, whereby iron and manganese are converted to their tri- and quadravalent states, resp., in which form they may be removed by filtration. At the same time dissolved free CO_2 and volatile odour and taste substances are expelled.

In the second step the water passes through an ozone-contact filter. Here the organic components which have not been expelled in the first step react with the ozone whilst the iron and manganese are removed at the same time by filtration, and the remaining excessive dissolved CO_2 is converted to carbonate. This filter is a combination of a closed "dry filter" and an ozone washer, where the usual ceramic packing is replaced by quartz gravel. The water passes through the large contact surface of the filter material in the presence of an ozone-containing air mixture, maintained slightly above atmospheric pressure. The ozone is almost completely stripped out and is used to oxidize the dissolved organic material. The exhaust air from the ozone contact filter is passed to the spraying tower where any remaining residual ozone is removed.

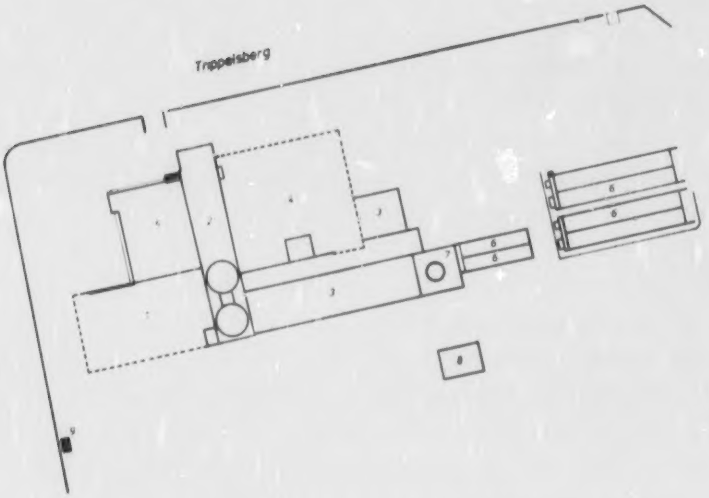
Trippelsberg
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Fig. 1

1 raw water tank
2 plant house with spraying tower
3 filter plant
4 pure water tank
5 auxiliary buildings
6 sedimentation tanks
7 sludge dewatering plant
8 reactivation plant
9 .natural gas regulating station

Offene Steilverdüsung - Ozon-Kontaktfiltration - Aktivkohlefiltration.

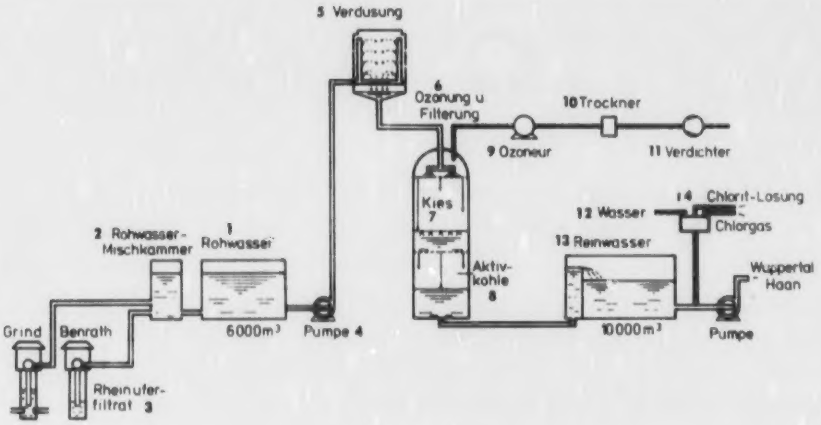

5 Verdusung
6 Ozonung u Filterung
10 Trockner
9 Ozoneur
11 Verdichter
Kies 7
14 Chlorit-Losung
12 Wasser
Chlorgas
13 Reinwasser
2 Rohwasser-Mischkammer
1 Rohwasser
Aktiv-kohle 8
Wuppertal Haan
Grind
Benrath
6000m³
Pumpe 4
10000m³
Pumpe
Rheinufer-filtrat 3

Fig. 2

1 Rohwasser: raw water
2 Rohwasser-Mischkammer: raw water mixing chamber
3 Rheinuferfiltrat: Rhine sandbank filtrate
4 Pumpe: pump
5 Verdüsung: sprinkler unit
6 Ozonung und Filterung: ozonization and filtration
7 Kies: gravel
8 Aktivkohle: activated carbon
9 Ozoneur: ozone generator
10 Trockner: drier
11 Verdichter: compressor
12 Wasser: water
13 Reinwasser: treated water
14 Chlorit-Lösung: chlorite solution

In the third step the water is passed through an activated carbon filter. This treatment step gives the water its final polishing by adsorption of organics, removal of residual ozone and odour and taste substances, and by biological degradation of ammonium ions.

The filters consist of 16 two-story units, the upper containing the ozone contact filter (dry filter) and the lower the activated carbon filter. The filters are constructed of prefabricated reinforced concrete and are pre-stressed in 3 axes. They have an inside width of 2.7 m and an internal length of 14.0 m, and each has a filter surface area of 37.8 m^2. The filter velocity is 12 m/h. A diagram of a filter is shown in Fig. 3.

The water distributors in the ozone contact filters consist of ring pipes equipped with so-called full jet spray nozzles which have a square spraying area. The spraying areas, arranged in a row, provide a uniform distribution of water in the filter.

Fig. 3: Cross-section of a filter, pipe-layout

From a distribution ring main the ozone-containing air is passed through flow meters to the filters, co-current with the water. The water level in the filters is kept constant below the filter support tray with the aid of an externally installed automatic float valve.

Activated carbon filtration is carried out in wet-filters.

Six tube generators are used for the production of ozone, each with a capacity of 2.5 kg/h, which give a total capacity of 15 kg/h. The plant allows an ozone dosage of up to 2 g/m^3 water. The exit air is then compressed with water-ring pumps. It is then passed through a water separator and two parallel, automatically operated cooling and drying columns, before reaching the ozone generators.

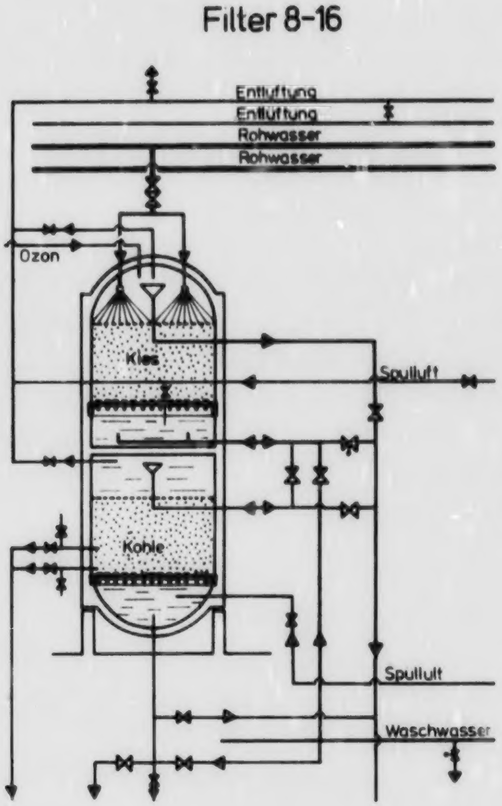

Filter 8-16
Entlüftung
Entlüftung
Rohwasser
Rohwasser
Ozon
Kies
Spülluft
Kohle
Spülluft
Waschwasser

Fig. 3

Entlüftung: ventilation
Rohwasser: raw water
Spülluft: backwash air
Kies: gravel
Kohle: carbon
Waschwasser: backwashing water

The backwash water from the filter is pumped to three sedimentation tanks. The thickened sludge is de-watered in chamber filter presses and is then disposed of.

Activated carbon regeneration

Method of regeneration

Under certain conditions, biological regeneration of the activated carbon in the filter can be of advantage, because a regeneration outside the filter is then only rarely necessary. However, this procedure has not been tested sufficiently to give generally valid information, and it may be that it can only be used in special cases.

It is also possible to use chemical regeneration where the adsorbed substances are removed from the carbon by extraction, using an organic solvent. However, in waterworks chemical regeneration creates problems because of the toxicity of the solvents and the difficulties inherent in their removal from the carbon.

It appears that thermal regeneration of activated carbon produces the least problems. Although the mechanism of regeneration has not been completely explored and there are still many tests necessary for the optimization of a regeneration plant, it can be said with certainty that such plants can be operated in waterworks.

Types of regeneration furnaces

For regeneration three main types of furnaces are used. These are the rotary kiln, the multiple-hearth furnace and the fluidized-bed furnace. On account of the experience already available, a fluidized-bed furnace was chosen for regeneration. In a waterworks, whose main task is not the regeneration of activated carbon, the operation of such a plant must be easy to perform by the existing staff. The fluidized-bed furnace meets these requirements to a large extent by the following characteristics:

- simple construction, no movable parts
- short start-up and turn-off periods due to low sensitivity against temperature changes
- simple supervision and control
- low losses in regeneration
- satisfactory efficiency

Regeneration at the Benrath waterworks - planning, tests, operation

The regeneration furnace

The projected furnace, a single-step fluidized-bed furnace, is designed to meet the following requirements:

throughput: 200 kg/h dry carbon, initial moisture 50 % water, final moisture 0 % water

bulk weight of the loaded wet carbon: 550 kg/m^3

granulation size of carbon: 0.5 to 2.5 mm

specific heat requirement of carbon: approx. 0.2 kcal/kg and 1 °C

temperatures: feed approx. 10 °C, finished product approx. 600 °C, combustion gases before the fluidized bed approx. 1000 °C, afterburning at approx. 900 °C, exhaust gases after afterburning approx. 500 °C

energy requirements: 115 m^3/h natural gas for the reactor including afterburning

current: approx. 30 kW; water: approx. 400 kg/h (liters/hr)

Figure 4 shows a schematic layout of the furnace.

The natural gas is stoichiometrically burnt in a superimposed combustion chamber, and the combustion gas is cooled down to the desired temperature by injection of water. The gas mixture enters the fluidized layer of carbon through a distributor ensuring even distribution.

Fig. 4: Regeneration furnace

The distributor tray is made of a refractory, compressed material with heat-resistant nozzles. No additional sections are provided for the fluidized layer because the tests, made with different types of activated carbon, produced in each case a satisfactory homogeneous regenerated material.

The furnace chamber widens above the fluidized layer. Due to the reduced gas flow velocity, this results in a stabilization of the fluidized layer on the one hand, and a limitation of the dust discharge on the other.

The dust granules discharged from the fluidized bed have a diameter of less than 0.2 mm. This dust would also be eliminated with the backwashing of the filters.

The retention time of the carbon in the furnace is dependent on the height of the fluidized layer at a constant rate of addition of carbon. The adjustable outlet weir allows a variation of ± 50 % in the height of the fluidized layer and thus also of the retention time. In addition, the retention time can be regulated by the rate of throughput.

The outlet temperature of the regenerated carbon is used as the normal set point for the process. At a constant throughput of fuel gas this temperature is stabilized by altering the speed of rotation of the feed screw.

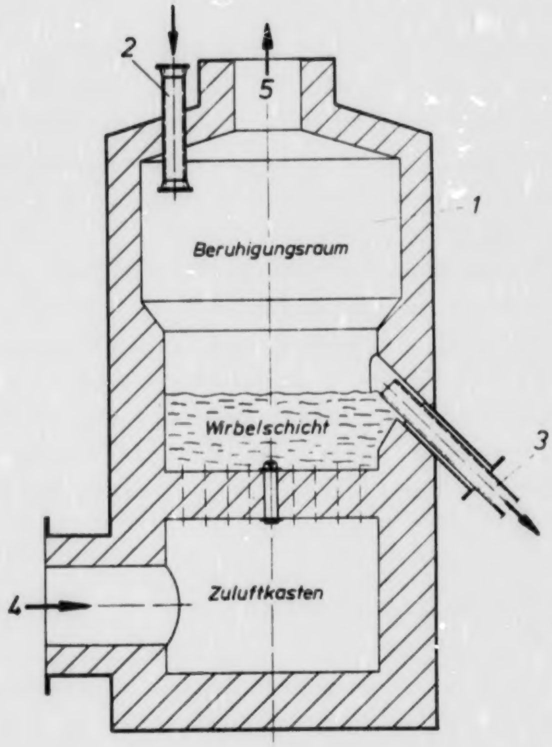

2
5
1
Beruhigungsraum
Wirbelschicht
3
4
Zuluftkasten

Fig. 4

1) Fluidized bed plant
2) product inlet
3) discharge and control for height of fluidized bed
4) flue gas inlet
5) flue gas outlet

Beruhigungs raum - Chamber for quieting gas flow

Wirbelsch icht - Fluidized bed
Zuluftkasten - Incoming air chamber

Fig. 5: Schematic layout of the regeneration plant

The furnace is connected with an afterburning chamber. The exhaust gas analyses obtained from the test reactivations and the regulations from the "TA Luft" (technical regulations for retaining air clean) make it necessary to provide for waste gas purification. This is shown schematically in Fig. 5.

The waste gas passes through a double cyclone before reaching the combustion chamber which is heated with an infinitely variable reaction burner. The furnace air is pre-heated in a heat exchanger by utilizing the heat content of the purified waste gas. Dust separation and afterburning guarantee that the quality of the waste gas meets the requirements of the "TA Luft", i.e. that the dust discharge is less than 75 mg/m^3.

Auxiliary plant, transport facilities

The regeneration plant is installed in its own building. As indicated in Fig. 6, the building consists of a reinforced concrete supporting structure with a light metal facing.

Fig. 6: Activated carbon regeneration plant building

Three rectangular concrete silos form one end of the building. The building is located in the waterworks in such a position that the transport distance for the carbon between the filter, the regeneration plant and the carbon discharge trays is as short as possible.

A schematic layout of the complete activated carbon system is shown in Fig. 7.

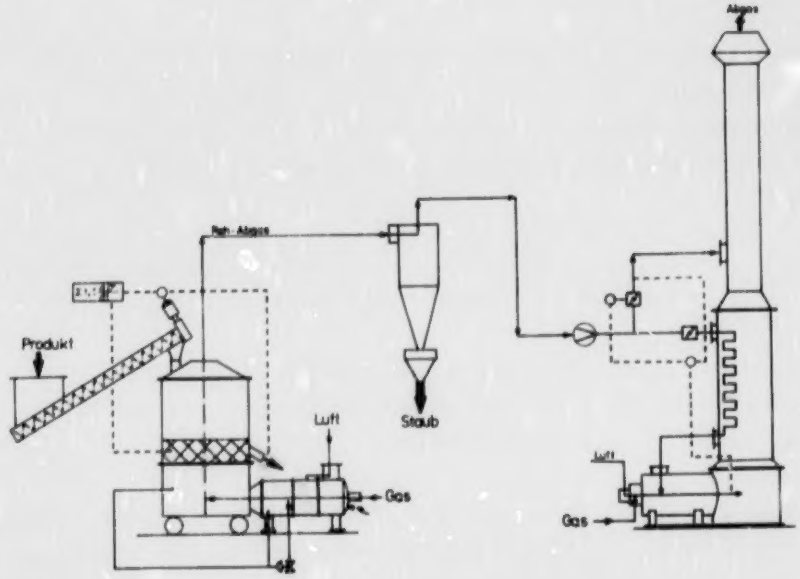

Abgas
Roh-Abgas
Produkt
Luft
Staub
Gas
Luft
Gas

Fig. 5

Roh-Abgas: flue gas

Luft: air

Staub: dust

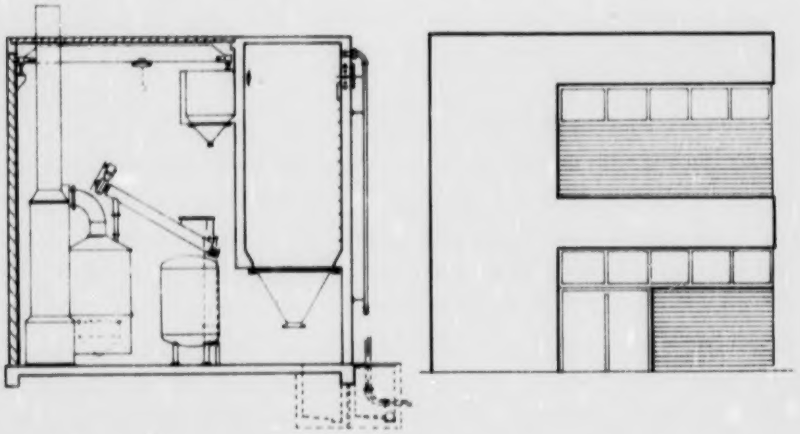


Fig. 6: Activated carbon regeneration plant building

The exhausted activated carbon is hydraulically transported from the filters to the activated carbon sedimentation tank. The tank simply acts as a buffer so that the time for backwashing and discharge processes can be kept as short as possible.

Fig. 7: Activated carbon regeneration plant with transport-, storage- and auxiliary facilities

The exhausted carbon is transported, using an injector, from the sedimentation tank to the exhausted carbon storage silo, a process normally taking one hour.

The exhausted carbon silo has, similar to the other two silos, a capacity of approx. 88 m^3 and can take the carbon from one filter. From the silo the carbon is hydraulically transported via a gravel-carbon-separator to an intermediate tank. In this separator the supporting gravel, carried with the carbon from the filter, is then separated from the exhausted carbon. This is necessary as the gravel interfers with the operation of the injectors and the regeneration furnace. The separator was especially developed for this purpose and produces a carbon product containing less than 0.5 % gravel.

The intermediate tank, of 8 m^3 capacity, acts as a storage tank for the feed screw on the regeneration furnace. With a regeneration capacity of 200 kg/h dry carbon, a buffer period of about 20 hours is obtained when there is no carbon feed. The de-watered carbon is then fed to the fluidized bed. After the regeneration process the reactivated carbon is cooled in a quenching- and wetting tank. The hot gas contained in the carbon contracts so that the cold water may easily fill the pores. The remaining gases are dissolved in water and the carbon is wetted. The available storage volume of the quenching tank gives a two-hour buffer period.

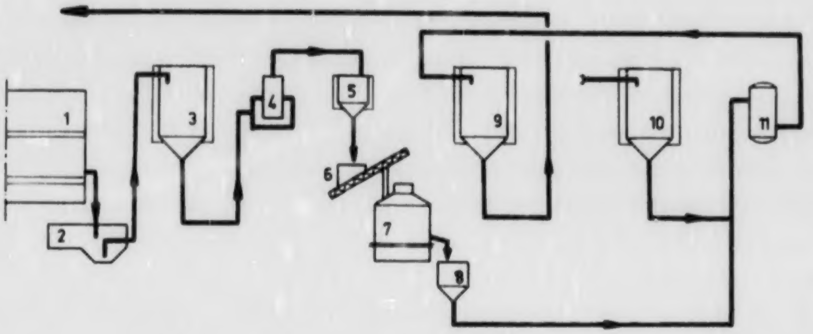


Fig. 7

1) activated carbon filter
2) sedimentation basin
3) storage tank for loaded carbon
4) separation plant
5) intermediate tank
6) conveying screw
7) high-temperature fluidized bed
8) wetting tank
9) tank for reactivated carbon
10) tank for new carbon
11) backwashing tank

From the quenching tank the reactivated carbon is conveyed by an injector to the washing tank, where the fine carbon particles are washed out. From the washing tank the carbon is transported to the reactivated-carbon silo. This silo provides the necessary buffer period of about 4 hours required for the filling of a filter with carbon.

In the third silo the new carbon - to replace that lost in regeneration - is stored. Before being used in a filter, the new carbon is wetted in the rinsing- and wetting tank where it is subjected alternatively to increased and to reduced pressure, and it is then passed to the reactivated-carbon silo where it is mixed with the other carbon.

The water used in the transport process is passed to a tank which has an internal volume of 30 m^3. Into this tank the water discharged from the containers carrying activated carbon is also passed. Any carbon carried in the water settles to the bottom of the tank, from where it is then passed to the exhausted-carbon silo by an injector. Finally, the water flows to the sludge sedimentation tanks.

The activated carbon is transported from the sedimentation tank to the silo for exhausted carbon in a stainless steel pipe, NW 125. The pipeline is coated with synthetic material and layed in such a way that it can be cleaned or freed from blockages without difficulty. The outer wall of the pipe bends, which have a large radius of curvature, are double-skinned to allow for abrasion wear. At the Düsseldorf waterworks they are lined with basalt.

The carbon washed into the sedimentation tank contains about 2 - 3 % gravel of various sizes, ranging from 0.7 to 10 mm. Since the gravel may interfere with the operation of the injector, a sludge pump is provided as an alternative. As the level of the carbon in the tank alters, the position of the sludge pump is shifted, using an electric hoist. The rate of discharge of carbon from the tank to the silo is adjusted by a suitable control system.

The speed of ascent of the activated carbon/gravel mixture entering the silo is kept below 1.6 m/h. Previous experiments have shown that, at a velocity of 10 m/h, activated carbon is washed out through the overflow pipe. During the filling process a gauge intermittently measures the height of the carbon in the silo. The measured value is transmitted to the sludge processing- and activated-carbon regenerator control panels. The filling process is switched off manually when the desired height of carbon has been reached.

Conveyance of the carbon from the silo to the intermediate tank, via the separation tank, is automatically controlled. When the minimum carbon level in the silo or the maximum carbon level in the intermediate tank are reached, the conveying process is halted. It re-starts automatically when a minimum level is reached in the intermediate tank. Contrary to this, when the level in the silo reaches a minimum value, the process has to be re-started by hand after the silo has been refilled.

With an intermediate tank filled with carbon and the wetting tank filled with water and after the desired furnace temperature has been reached, the feeding screw is automatically started and carbon is fed into the furnace. The intermediate tank is filled automatically, controlled by an impulse contactor. If the filling process is interrupted the feed to the furnace is continued for another hour, then the furnace is switched off, having received optical and acoustical signals. Only when the intermediate container has been refilled can the furnace be restarted, either automatically or by hand.

An alternative example of the external storage and transport of activated carbon is provided by the Düsseldorf waterworks. Here silo trailers are used for the intermediate storage and transport between three waterworks, in addition to the fixed silos. The transportable silos can be connected to any fixed silo. They are also used for the transport of exhausted and regenerated carbon. A schematic layout of this plant is shown in Fig. 8.

Fig. 8: Transport system, external storage
(Düsseldorf waterworks)

The processing tests for the separation of gravel and carbon led to the installation of continuously operating separation equipment. The separator is filled by hand before the gravel/carbon mixture is introduced through two diametrically opposed feed pipes, and is at the same time automatically vented. The gravel separates from the carbon due to the different settling velocities of the two materials. The activated carbon slowly fills the separator and is removed through a pipe at the top of the separator. When the gravel has reached a maximum level in the separator, it is removed (see Fig. 9).

Fig. 9: Gravel/carbon separator

Here the E-armature exit pipe is automatically opened by a radioactive sensor and is closed after gravel removal is complete by a second sensor. If there is an interruption during gravel removal there is the danger that gravel is carried with the carbon to the furnace. Therefore a time relay gives an optical and acoustical signal when the maximum gravel level is maintained longer than a set time.

The separator has a diameter of 800 mm and a height of 1850 mm. The base is fitted with nozzles, 100 per m^2.

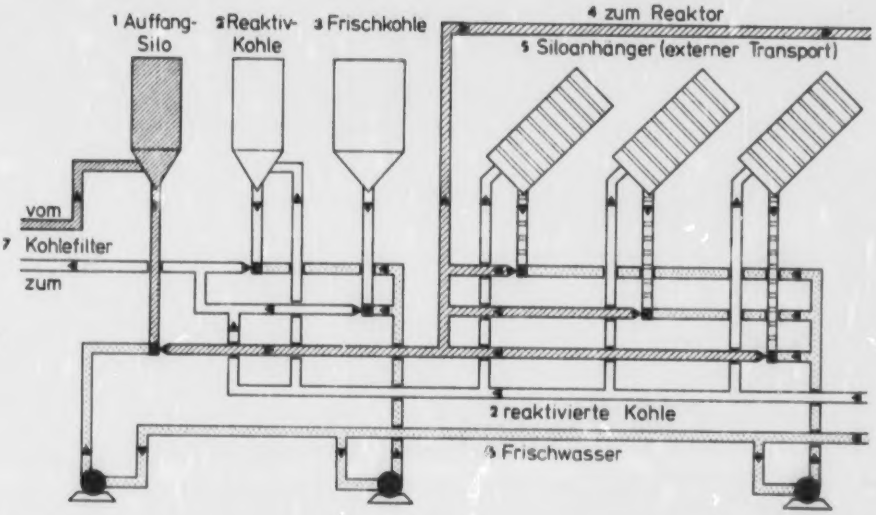

1 Auffang-Silo
2 Reaktiv-Kohle
3 Frischkohle
4 zum Reaktor
5 Siloanhänger (externer Transport)
vom
7 Kohlefilter
zum
2 reaktivierte Kohle
6 Frischwasser

Fig. 8

[1]Auffang-Silo : receiving silo

[2]Reaktivkohle : reactivated carbon

[3]Frischkohle : fresh carbon

[4]zum Reaktor : to the reactor

[5]Siloanhänger : silo trailer (external transport)

[6]Frischwasser : fresh water

[7]

vom/zum Kohlefilter: from/to activated carbon filter

activated carbon - reactivation plant - transport system -

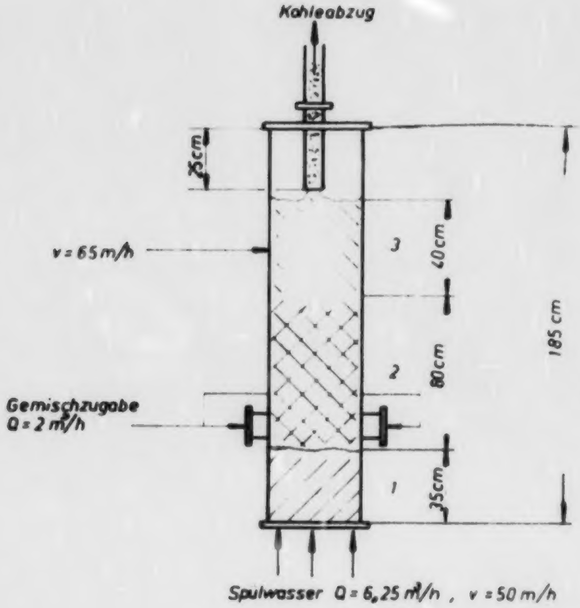

Kohleabzug
25cm
v = 65 m/h
3
40cm
2
80cm
185 cm
Gemischzugabe
Q = 2 m³/h
1
35cm
Spulwasser Q = 6,25 m³/h , v = 50 m/h

Fig. 9

Kohleabzug : carbon outlet
Gemischzugabe: mixture feed
Spülwasser : backwash water

New carbon is supplied in a silo-transporter. The hose of the silo-transporter is coupled to the fresh-carbon silo injector. The silo volume has been designed so that it holds the contents of several transporters, which at the same time ensures that unwetted carbon is not carried away with the overflow water.

During the filling process a sensor measures intermittently the filling height of the carbon. This data is transmitted to the control panel of the carbon regeneration plant. When the silo-transporter is empty, the filling process is switched off manually. After completion of the filling the water supply valve is opened and the water rises up to just below the overflow level, the level being controlled by a float valve. After some days the carbon is superficially wetted. The final wetting is carried out under pressure in the flushing and wetting tank.

As already described, between 200 l/h (normal) and 400 l/h (maximum) of water are required for the regeneration furnace as spray water for the regulation of the temperature of the combustion gases. On account of its composition, the water has to be processed with an automatically operated quality-controlled water softener. The regeneration of this plant is also carried out automatically.

Because they may cause trouble in practice, some "groups" of problems concerning the auxiliary plants are to be mentioned separately. For feeding equipment there was the choice of injectors, channel impeller pump, feed containers, feed screws. The feeding of the water-activated carbon mixture, at a rate of 3 : 1, was to be undertaken with as low a wear and tear as possible and at a low energy expenditure. Of most advantage seems to be the use of injectors because they show the least wear. In addition, water with the required pressure is available to operate the system.

The channel impeller pump causes an increased abrasion of the feeding material and is itself subjected to wear and tear. When used in a container, the re-adjustment of the pump requires an increased technical effort. In addition, electrical energy is required.

Feeding containers operate intermittently. This method is also low in wear but has not been sufficiently tested.

The feeding screw undertakes the important task of providing the reactor with a constant supply of activated carbon while at the same time separating the carbon from the water and providing an air-tight seal. For this purpose, attention must be paid to the setting angle, the clearance number of turns, the pitch and the rotational speed. If it is incorrectly constructed, the moisture content of the carbon will be too high, or the feed rate of the carbon insufficient, or the attrition of the carbon will be too high. All this will affect the regeneration process. Figures 10, 11 and 12 show some data on the feed screw performance, the effect of rotational speed on water content (which also depends on the type of carbon), and of the slight size reduction of the granules caused by the feeding process.

Fig. 10: Capacity of the feed screw

Fig. 11: Water content of conveyed activated carbon, dried at 110 °C, 24 hours

Fig. 12: Attrition test of activated carbon after repeated passage through the feed screw

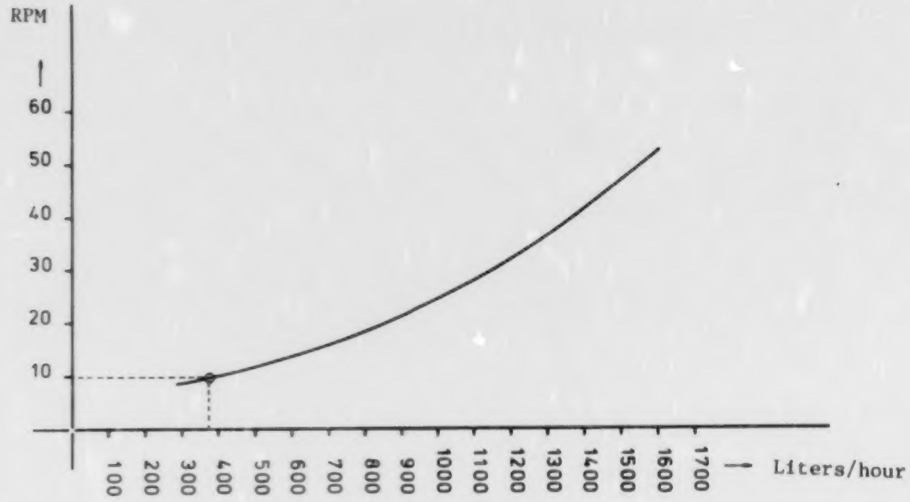


Fig. 10 Capacity of the feed screw

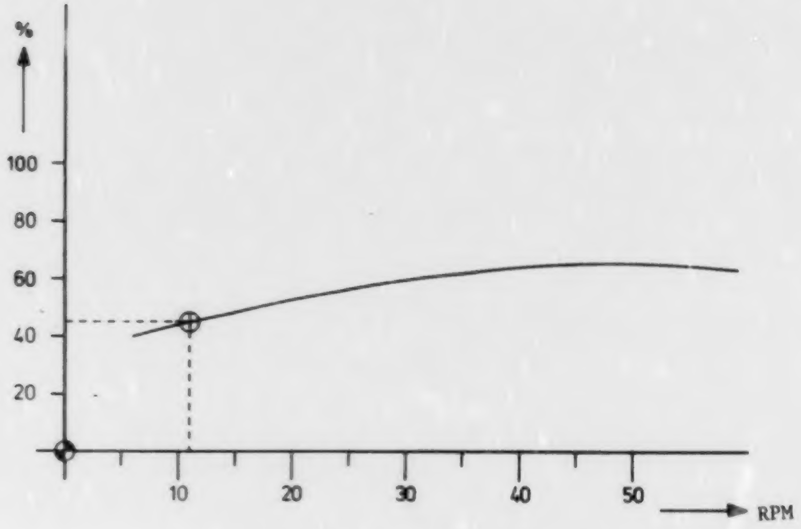


Fig. 11: Water content of conveyed activated carbon, dried at 110 °C, 24 hours

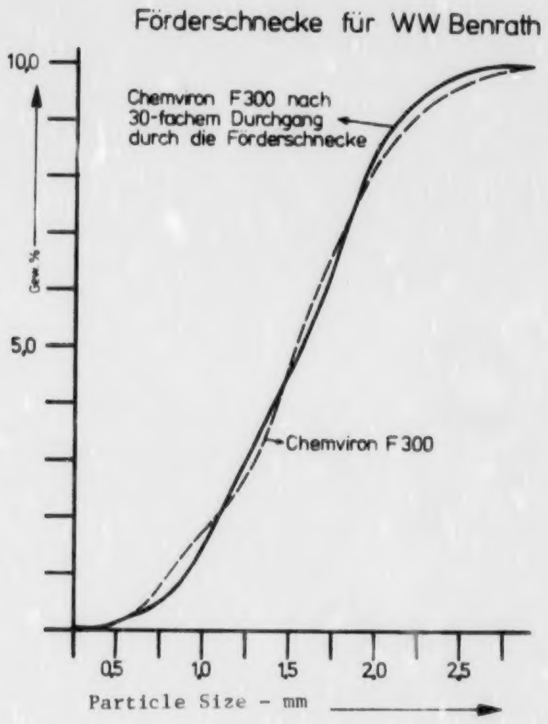


Fig. 12

Förderschnecke für WW Benrath: conveying screw for Benrath waterworks

Chemviron F300...: Chemviron F300 after passing through the conveying screw for 30 times

Gew.-%: weight per cent

It has been found that stainless steel was the most suitable material for containers and pipe bends which come into contact with activated carbon. In addition, it is corrosion-resistant and has a good coefficient of friction. For straight pipe pieces synthetic material is sufficient.

The velocity of the water/carbon mixture in the pipelines can only be varied within certain limits. If the velocity is too high, there is a high abrasion of the carbon and wear of the pipelines, while if the velocity is too low carbon is deposited, which leads to blockages. Experience shows that velocities between 1.5 m/s and 3 m/s are free from interference.

Continuous measurement of the quality of the regenerated material is also a problem, which is being investigated at many places including the Engler-Bunte-Institute at Karlsruhe. Of particular interest is a simple and rapid control method for the operator which, circumstances permitting, could be used to control the operation of the regenerator. The present regeneration tests consist of measuring the bulk weight, the hardness, the ash content and the benzene load for volume ratios of 9/10, 1/10 and 1/100. In addition, isotherms are determined by UV extinction at 254 nm and compared with the values of new carbon. Also the methylene-blue number and the molasses factor are used for further evaluation. Some test results are shown in Fig. 13 and Table 1. In addition, in Table 1 screen analyses are shown of the distribution of granule sizes with the number of regeneration cycles.

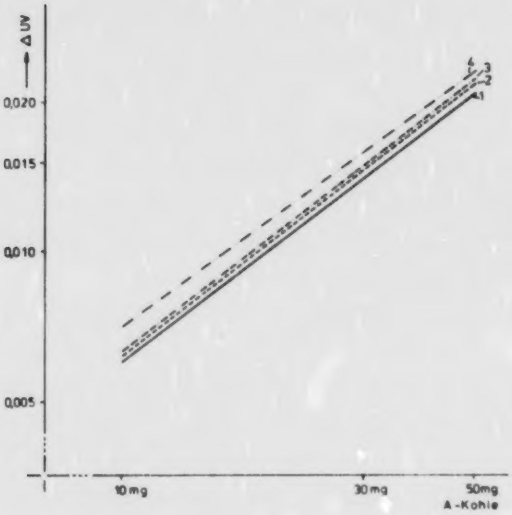


Fig. 13: Adsorption isotherms after repeated regeneration

1 - isotherm new activated carbon
2 - isotherm after first reactivation
3 - isotherm after third reactivation
4 - isotherm after fifth reactivation

Table 1: Comparison of new and regenerated activated carbon

Measuring procedure: 1 l water + 10/30/50 mg powdered activated carbon is stirred for 2 h at 70 rpm. It is then centrifuged and the UV adsorption is measured at 254 nm in a 1 cm cuvette.

Probe	F 300 Neu	F 300Reaktivat 1xreaktiviert	3xreaktiviert	5xreaktiviert
Schuttgewicht kg/l	0,485	0,480	0,490	0,490
Siebanalyse Gew %				
> 3,15mm	0,5	0	0	0
2,00 – 3,15mm	26,0	24,3	20,1	10,3
1,25 – 2,00mm	40,0	39,7	44,0	48,0
0,80 – 1,25mm	29,1	27,1	27,4	31,6
< 0,80mm	4,4	8,9	8,5	10,1
Harte in Gew %	98,9	95,0	93,5	91,8
Benzolbeladung Gew %				
1/10	28,5	29,0	28,2	26,5
9/10	33,0	34,9	34,3	33,9
Aschegehalt Gew %	4,2	5,2	6,8	8,2
UV-Adsorption 254nm/1cm Kuvette				
0 mg	0,039/ΔUV	0,039/ΔUV	0,039/ΔUV	0,039/ΔUV
10 mg	0,033/0,006	0,033/0,006	0,033/0,006	0,032/0,007
30 mg	0,025/0,014	0,024/0,015	0,024/0,015	0,023/0,016
50 mg	0,018/0,021	0,017/0,022	0,018/0,021	0,016/0,023

Table 1

Schüttgewicht: bulk density
Siebanalyse: grain size
Härte in Gew%: hardness in weight per cent
Benzolbeladung: benzene loading in weight per cent
Aschegehalt: ash content in weight per cent
Probe: sample
F 300 neu: F 300 new
reaktiviert: reactivated

Economics

The planning was preceded by an investigation of the economics of the regeneration process. Taking as a basis a regeneration plant with a throughput of 5 t/d, it was found that the plant was sufficiently utilized when the annual throughput is of the order of 1000 tons per year.

On-site regeneration was estimated at about 400 DM/t, compared with 1000 DM/t when regeneration is carried out at another plant. This means that the investment of about 2 million DM for the regeneration plant will amortize quickly.

The calculations, which have to be compiled for each individual works, take into account: regeneration costs at an outside firm, transport costs, regeneration and transport losses, energy costs, labour and maintenance costs, servicing of investment.

With regard to the investment costs, it must be remembered that particularly in the case of plants with a capacity of up to 5 t/d there is a rapid reduction in the specific cost. However, with larger plants the specific costs diminish only slightly. The following values were used:

Natural gas : 0.16 DM/m^3
Electricity : 0.10 DM/kWh
Investment service: 11 per cent
Shift length : 9 h/d
Maintenance costs : 5 per cent of the investment on machinery and transport system

The losses during regeneration were estimated at 5 per cent, and the total losses (including transportation) at approx. 15 per cent.

Final considerations

A report on the experience and the actual operation of a regeneration plant can only be made after the plant has been in operation for several months. Although it means a new departure for a waterworks, due to the experience gained with pilot plants and existing plants, sufficient safety is guaranteed for a fault-free operation of the plant and its economics.

The special advantages of a waterworks having its own regneration plant are as follows:

1. To be in a position to satisfy at any time an increased demand for activated carbon.

2. To be able to adjust the regeneration of the activated carbon to the particular requirements to an optimum extent, and to obtain a satisfactory regenerated material.

Finally, all these efforts serve the endeavour to supply the public with an acceptable quality of drinking water.

INVESTIGATIONS CONCERNING THE MICROBIOLOGY OF ACTIVATED CARBON FILTERS

by M. Klotz, P. Werner, R. Schweisfurth, of Homburg/Saar

Introduction

Activated carbon is used to an increasing extent for the processing of drinking water from surface- and ground waters - and perhaps even from wastewater in the future. Practical experience has shown that there is a mass increase of micro organisms (bacteria and fungi) in the carbon filters and also in the filtrate.

Almost nothing is known of the basic factors controlling the formation of a micro flora, its activity, numbers, species and composition in the system under discussion, i.e. flowing water of varied chemical composition and activated carbon. In addition, little is known of the influence of the micro organisms on adsorption and desorption.

Investigations on this problem reported in this paper were carried out in close cooperation with several waterworks; the keypoint was at the Rhine-water treatment plant at Wiesbaden-Schierstein, whose equipment and facilities were used.

Methods

From a methodical point of view, the definition of the amount of micro organisms in the water presents no difficulty if, after an adequate pretreatment, nutrient media, breeding temperature and breeding time are suitably chosen.

The definition of the colony numbers present in the water, as recommended by "DEV" (Deutsche Einheitsverfahren = German Standard Methods) proved to be inadequate for our investigations because only a small part of the micro flora is covered by this method. As expected, all nutrient media tested showed considerably increased colony numbers after breeding for seven days, than after breeding for two days. The best media for a quantitative coverage of micro organisms was found to be P-Agar which

contained few nutrients (WOLTERS,1956) and SPC-Agar which was rich in nutrients (STANDARD METHODS 1966), both were incubated at 27 °C for more than 7 days. The colony numbers shown in Fig.1 refer to the medium rich in nutrients. The activated carbon was crushed in a simple mixer and the homogenized material was then processed for the determination of the colony numbers in the same manner as water samples.
The cell number, i.e. the total number of all living and dead bacteria, was determined by microscopical counting after accumulation on the membrane filters and colouring.
Apart from a few modifications, the tests were carried out as recommended by D E V whenever possible.

Fig.1: Annual mean values of colony numbers of bacteria in dependence of the treatment steps at the Rhine-water processing works at Wiesbaden-Schierstein (obtained from SPC-Agar after an incubation of 7 days.

Results

1. Quantitative coverage of the population of micro organisms

1.1 Survey of the colony numbers in the different treatment steps

For a better understanding of the work presented below, it is necessary to know the method of treatment used at the Wiesbaden works, where Rhine-water is pretreated before infiltration for an artificial augmentation of the ground water. The water is taken from the river, aerated, plain settling , after which it is chlorinated and flocculated. Then follows a rapid filtration through sand and activated carbon before the water is infiltrated into the underground. In Fig. 1 the mean values of the colony numbers are given from March 1973 to March 1974. There is a decrease of the colony numbers between the Rhine and the entrance to the carbon filter (sand filtrate). The biggest effect is achieved by the break-point chlorination. Fresh populations of micro organisms are formed in the activated carbon filters, so that very high colony numbers can be traced at the filter exits using the special method. Using the methods normally applied for the definition of colony numbers, as recommended by the DEV for the control of drinking water, the water quality is satisfactory as a rule.

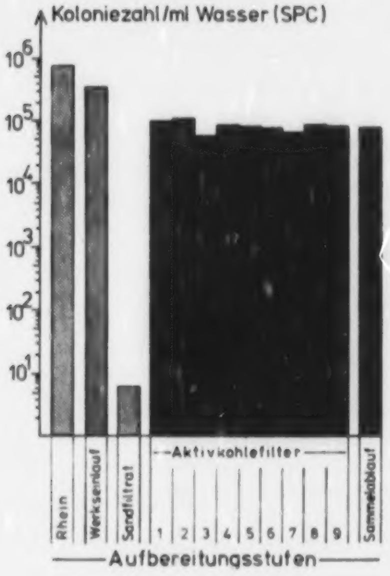


Fig. 1

Aufbereitungsstufen: treatment steps

Koloniezahl/ml Wasser: colony numbers/ml water

Werkseinlauf: works inlet

Sammelablauf: collecting outlet

Aktivkohlefilter: activated carbon filter

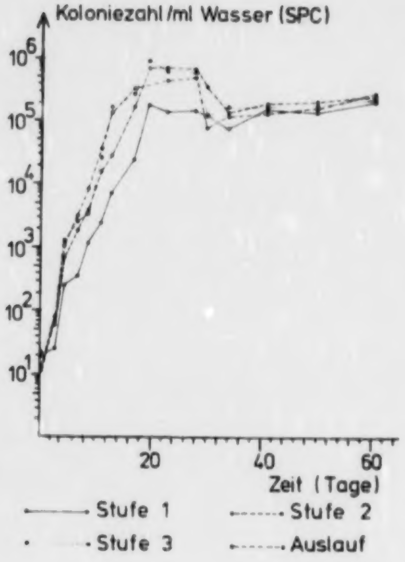
Sandfiltrat: Sand filter effluent

1.2 Composition of micro organism populations in an activated carbon filter

The composition of these populations was examined in freshly filled large filters and test plants. The test plant was dimensioned as follows: 4 successive glass tubes with an inside diameter of 4 cm. Layer height of the activated carbon bed 3.2 m (4 x 0.8 m). The behaviour of the micro-organism populations was found to be the same in both the test- and in the large filters. Passage of water through each individual filter is called a "filter step."
Within the first 20 day the colony numbers reached a maximum - after a linear increase - of 10^5 to 10^6/ml of water, after which they declined and remained at a slightly lower level (see Fig.2). In the beginning there were large differences at times between the individual filter steps, which disappeared after about 30 days after the level phase had been reached. Examination of the formation of the micro organism populations on the carbon show that the characteristics described above for the conditions present in the water are not very marked (see Fig.3). Because the inflowing water contains bacteria, the originally germ-free carbon has high initial colony numbers. They reach values of 10^6 to 10^7/g of wet activated carbon after some time.

Fig.2: Composition of micro organism populations in a test filter (colony numbers in the water obtained on SPC-Agar after 7 days' incubation)

Fig.3: Composition of micro organism populations in a test filter (colony numbers on the carbon obtain on SPC-Agar after 7 days' incubation)



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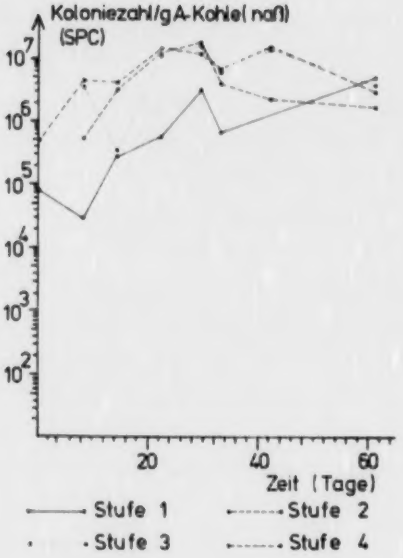

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Fig. 2,3

Koloniezahl/ml Wasser: colony numbers/ml water

Zeit (Tage) : time (days)
Stufe: step
Auslauf: outlet
Koloniezahl/g A-Kohle (naß): colony number/g activated carbon (wet

1.3 Influence of the filter velocity on the construction of the population

Based on the filter velocities used at the Rhine-water processing works, a range of 4 to 20 m/h was chosen for the test plants. The slope of the curves during the initial phase (see Fig.2) decreases with increasing velocity and with increasing filter length. The maxima are more pronounced as the velocity decreases. At the level stage there are only slight differences, the colony numbers are lowest with the lowest velocity.

1.4 Microbiological and chemical conditions in an operating large filter

With the aid of a characteristic individual test, the conditions as they are typical for an operating large filter are to be illustrated.

In Fig. 4 the colony numbers, the cell numbers and the content of free chlorine are shown as functions of the filter length.

Fig.4: Colony numbers (obtained on SPC-Agar after 7 days incubation), cell numbers and content of free chlorine in dependence of the filter length in a large filter.

The behaviour of the measured values up to step 2 can be explained by the small filter height and the lack of contact with the activated carbon. The largest increase of colony numbers takes place between steps 2 and 3; there is no further increase between step 4 and the outlet.

The evaluation of the colony numbers includes only fractions of the cell numbers. The increase of the cell numbers is, according to the total amount, similar to that of the colony numbers. The cell numbers from the inlet to step 2 represent dead bacteria.

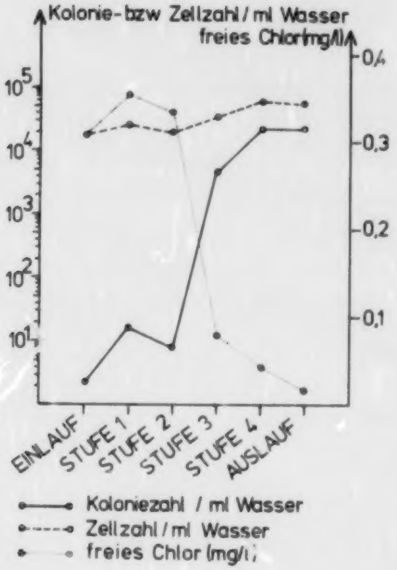


Fig. 4

Kolonie- bzw.Zellzahl/ml Wasser : colony- and cell number, resp.,/ ml water

freies Chlor: free chlorine

Sauerstoff: oxygen; Einlauf: inlet; Auslauf: outlet; Stufe: step

Koloniezahl /ml Wasser: Colonies/ml water

Zellzahl/ml Wasser: cell numbers/ml water

In the uppermost carbon layers the chlorine content falls below 0.1 mg/l, where it no longer has any perceptible influence on the increase of bacteria.

Anindicator for microbial activity is the change in the oxygen- and carbon dioxide content of the water, as shown in Fig. 5. During the filter passage there is an oxygen consumption of approx. 1.5 mg/l and at the same time there is a production of carbon dioxide of approx. 4.5 mg/l (to be compared with Table 2).

Fig. 5: Content of oxygen and free carbon dioxide in dependence of the filter distance in a large filter

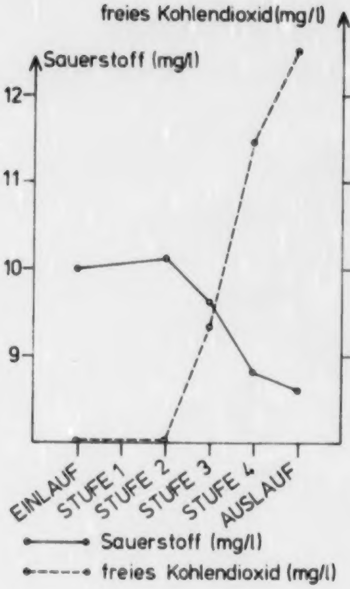
The change of the content of organics is illustrated in Fig. 6 by three parameters. In the case of the UV adsorption at 240 nm and of the DOC the values decreased by about 55 % after the filter passage, and by about 45 % in the case of $KMnO_4$.

Nevertheless, the change in degradability during filter passage is slight, as the results of BOD_2-, BOD_5- and BOD_{20} evaluations show. The degradability of organics is also slight; this must be taken into account when evaluating the activity of micro organisms.

Fig. 6: Content of organics in dependence of the filter length in a large filter

1.5 Behaviour of populations during a period of 3 years

The influence of the season and of the raw water on the micro organism populations in the treatment steps at the Rhine-water processing works was studied for several years. In Fig. 7 the relations for 3 characteristical steps are presented: works inlet (Rhine-water after aeration and basin passage), carbon filter inlet (sand filtrate) and carbon filter collecting outlet (infiltration water).



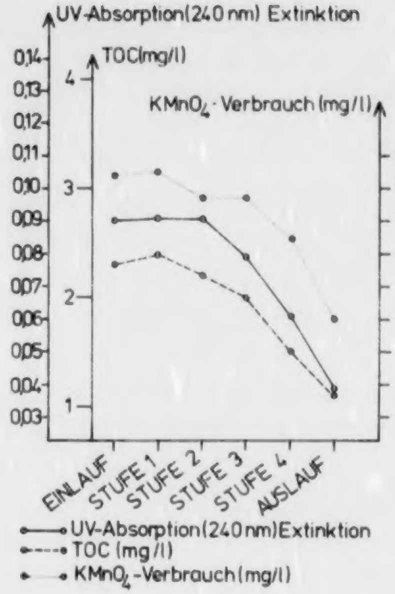


Fig. 6

Fig. 5

freies Kohlendioxid (mg/l): free carbon dioxide (mg/l)

$KMnO_4$-Verbrauch (mg/l): $KMnO_4$ consumption (mg/l)

Sauerstoff: oxygen; Einlauf: inlet; Auslauf: outlet; Stufe: step

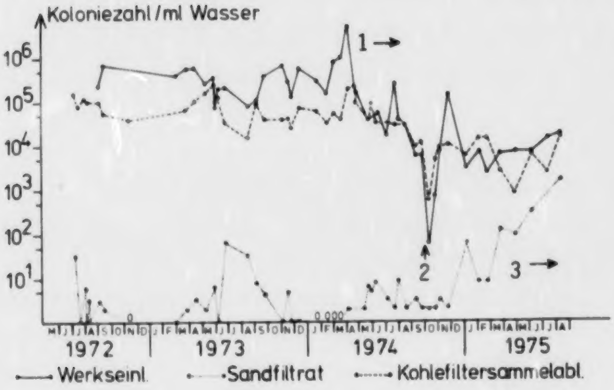


Fig. 7

Werkseinlauf: raw water inlet

Kohlefiltersammelablauf: carbon filter collecting outlet

Sandfiltrat: sand filtrate

The special methods under discussion, developed for the determination of the bacteria number - particularly after a long incubation time of 7 days - are much better suited for a quantitative determination of the micro organism populations than the hygienic-bacteriological methods according to DEV.Using this method,very high colony numbers were traced in the water of the works inlet and of the carbon filter collecting outlet. No conclusions can therefore be drawn from the colony numbers given here on the hygienic-bacteriological quality of the waters according to the present standard for drinking water. If these waters are examined using the method prescribed by DEV it appears that only the works inlet (i.e. the raw water) contains equally high colony numbers, but that the carbon filter collecting outlet meets the respective requirements. In this connection it must be pointed out that tests carried out at five German waterworks,using different treatment modes and different raw water qualities,similar differences with the results of the determination of colony numbers were found by using the special method described above as compared with the methods of the DEV. In all tested cases the outlets of the activated carbon filters showed similarly high colony numbers. Similar observations have been reported by scientists in Switzerland and the Netherlands.

Of some interest are also the efforts being made,aiming at employing the micro organisms in the activated carbon filter to improve the water - as against the previous intention to destroy them. The conditions at Wiesbaden-Schierstein are as follows: the influence of the seasons on the extent of colony numbers is slight; however, there seems to be a tendency for a decreased microbial activity in winter, as indicated by the chemical data (oxygen consumption, carbon dioxide production.

Changes in the water quality (marked by 1 to 3 in Fig. 7) resulted in a distinct change of the colony numbers.

2. Activity of the micro organism populations in the activated carbon filter

The problem of finding out to which extent the micro organisms were responsible for the change of substances and/or their decrease during filtration was solved by a comparison between a sterile and an unsterile operated test filter plant. Parallel with the large filters, two pilot plants consisting of 4 series-connected glass tubes with an inside diameter of 6 cm were operated under similar conditions. The layer height of the activated carbon bed was 2 m (4 m x 0.5 m). One of the plants was kept free of germs by sterile filtration for more than two months at a filtrate amount of 15 m^3. All the other methods of keeping the plant sterile have the disadvantage of the presence of an additional bactericidal substance and of a large number of dead micro organisms.

In order to increase the amount of degradable organic substances the inlet was loaded with about 50 mg/l phenol during the second part of the test, by retaining the previously used activated carbon.

Results of these tests are given in Tables 1 and 2. When the filter inlet is unloaded (sand filtrate) the share of the micro organisms in the decrease of organics is very small - as far as it can be measured by UV adsorption, DOC and $KMnO_4$ consumption. On the other hand, the share of the micro organisms in the decrease of easily degradable organics is high. This is of special importance because it means that the regrowth of bacteria that usually occurs in the distribution system now occurs in the waterworks itself.
When the inlet is loaded with phenol the activity of the micro organisms is slightly greater; it must be remembered, however, that the adsorption capacity of the carbon was very high for phenol.

Table 1: Percentage share of micro organisms in the removal of organic substances during activated carbon filtration

Table 2: Percentage share of micro organisms in oxygen consumption and carbon dioxide production during activated carbon filtration

Rohwasser / Parameter	Durchschnittlicher Anteil der Mikroorganismen an der Entfernung von organischen Substanzen	
	Sandfiltrat	phenol-belastetes Sandfiltrat
DOC	<1,0 %	6,0 %
$KMnO_4$ - Verbrauch	3,7 %	3,1 %
UV-Absorption 240 nm	<1,0 %	2,8 %
UV-Absorption 254 nm	1,2 %	6,2 %
BSB_2	69 %	-
BSB_5	46 %	-
BSB_{20}	17 %	-

Table 1

phenolbelastetes Sandfiltrat: phenol-loaded sand filtrate

Sandfiltrat: Sand Filter Effluent
Durchschnittlicher...Percentage share by microorganisms in the removal of organic substances during activated carbon filtration.
Rohwasser: Raw water
$KMnO_4$ Verbrauch: $KMNO_4$ Consumption
BSB_2: 2 Day BOD
BSB_5: 5 Day BOD
BSB_{20}: 20 Day BOD

Rohwasser / Parameter	Durchschnittlicher Anteil der Mikroorganismen	
	Sandfiltrat	phenolbelastetes Sandfiltrat
Sauerstoffverbrauch	58 %	68 %
Kohlendioxidproduktion	61 %	64 %

Table 2

Sauerstoffverbrauch: oxygen consumption
Kohlendioxidproduktion: carbon dioxide production

Durchschnittlicher...Percentage share by microorganisms
Phenolbelastestes Sandfiltrat: Phenol-loaded sand filtrate

Sand Filtrat: Sand filter effluent

3. Distribution of micro organisms in the system water-carbon

3.1 Electron-scan microscopic examination of the filter granule

During the filter passage the micro organisms increase from about 10 colonies/ml to about 10^5 colonies/ml. The doubling period for bacteria is around 20 minutes, even at the optimum environment conditions. This leads to the conclusion that, because the water remains in the filter for a short time only, the increase of micro organisms has to emanate from the bacteria on the activated carbon.

Tests have shown that there are colony numbers of up to 10^8/g of wet material on the carbon. The actual cell number, obtained by cell counting, can exceed these numbers by almost 100 %.

A variety of electron-scan microscopic tests of differently treated activated carbons produced a general view of the distribution of micro organisms on the filter granule: as a rule, the micro organisms are sparsely scattered, they are always in the form of a single bacterial layer; the area available (carbon surface up to a pore diameter of 1 μm) is only fractionally utilized (about 1 %). This is even the case when the carbon had been put into a nutrient solution for some time.

3.2 Tests on the adsorption of micro organisms onto activated carbon

It seems reasonable to explain the adhesion mechanisms of the micro organisms onto activated carbon by the adsorption processes. Investigations on the adsorption of micro organisms onto activated carbon were made using starved and washed bacteria (mixed populations) in a nitrogen-free environment.

Fig. 8 shows an adsorption isotherm, carbon load of bacteria in dependence of the adsorptive concentration. At high colony numbers (larger than 10^{10}) the system tends towards saturation. At numbers around 10^7 and 10^8 up to 90 % of the bacteria are adsorbed.

The investigation of the influence of time on adsorption proved to be difficult (see Fig.9). Despite extensive precautions, it is impossible to avoid increase and extinction processes over a longer period (dashed curve). After an incubation period of 20 to 30 hours adsorption and desorption are nearing a steady state. With increasing ion concentration (phosphate buffer pH 7.2) the bacteria loading of the carbon increases as shown in Fig.10. No dependence of the adsorption on the temperature in the range of 5 - 37 °C and of the pH value (pH 5-8) was noted. Dead bacteria are slightly better adsorbed than living bacteria.

Fig.8: Loading of activated carbon with micro organisms in dependence of the adsorptive concentration

Fig.9: Loading of activated carbon with micro organisms in dependence of time

Fig. 10: Loading of activated carbon with micro organisms in dependence of the ion concentration

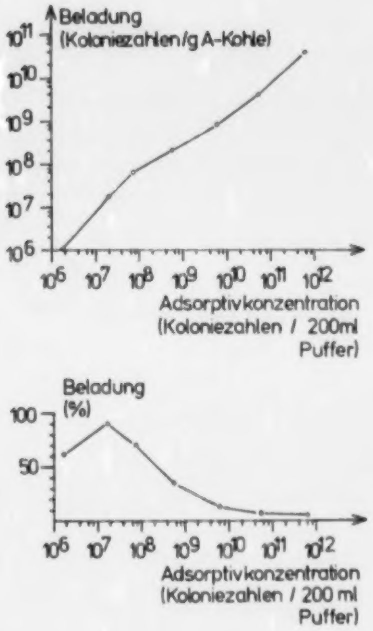
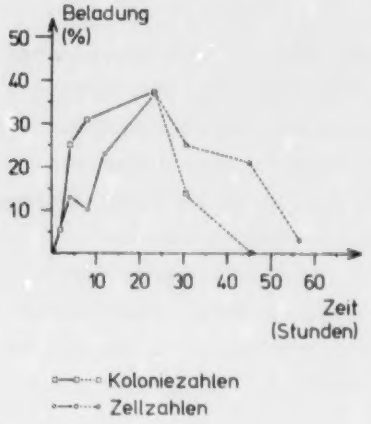


Fig. 8

Beladung: loading

Puffer: buffer
Koloniezahlen: colony numbers

A-Kohle: activated carbon
Adsorptivkonzentration: adsorptive concentration



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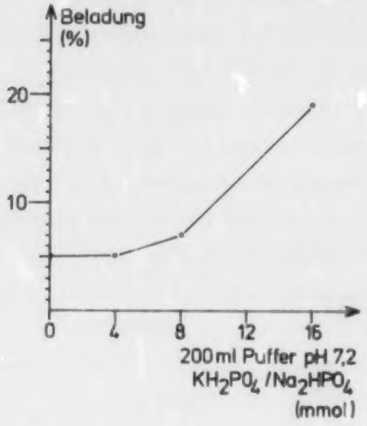

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Fig. 9,10

Beladung: loading

Zeit (Stunden): time (hours)

Puffer: buffer

Koloniezahlen: colony numbers

Zellzahlen: cell numbers

Discussion and Results

When activated carbon is used for the treatment of drinking water there is always a growth of micro organisms on the filter granules. Depending on the eco-system the micro organisms are insufficiently counted when using the DEV method. This made it necessary to develop a special method for the quantitative coverage of micro organism populations. As a rule, the water can be declared satisfactory, according to the present standards for drinking water. This growth was noted by several waterworks in Germany, irrespective of the method of treatment; it cannot be avoided by any of the treatment methods used for the processing of drinking water.

After a short synthesis phase the micro organism populations reach high colony numbers, which can only be measured by special methods; after that, the numbers remain constant for a long time. Changes in the composition of the water have an influence on these numbers.

The micro organisms contribute to the purification of the water by their activity, which is not only indicated by colony numbers. This contribution depends not only on the quantity of organic substances but also on their quality and especially on their degradability. Inorganic as well as organic substances are changed or degraded.

The activity of the bacteria is also influenced by their number, their distribution and their retention time in the water-carbon system. These parameters are mainly influenced by adsorptive processes.

The research programme will be continued by carrying out investigations on the qualitative definition of the flora of micro organisms and on the influence of activated carbon on their metabolism.

EXPERIENCE WITH THE USE OF BIOLOGICALLY EFFECTIVE ACTIVATED CARBON

by M.Eberhardt, Bremen

1. Introduction

This report covers the mineralization of organic substances during the treatment of surface waters by using biologically operating activated carbon filters. Almost no practical experience is available at present on the use of such filters in a large waterworks plant. Our experience is limited to relatively small pilot plant filters which have been in operation for several years. A simultaneously operated slow filter plant makes it possible to compare the results and conclusions drawn.

Water from the river Weser which had been pre-cleaned by flocculation and rapid sand filtration - the so-called rapid filtrate - was treated in four successive test filters, each having a layer height of 1.5 m. The total layer height of the filters amounted therefore to about 6 m. For comparison, four other filters, provided by courtesy of the Lurgi company, were operated in parallel with different types of activated carbon. In addition, a second pilot plant with a layer height of 3 m was used for the tests with ozone pretreatment. Detailed reports on the test plants were made on previous occasions (EBERHARDT 1971; EBERHARDT, MADSEN, SONTHEIMER 1974 and 1975). As a first step, some theoretical considerations are to precede the discussion of practical test results.

2. Mineralization of organic substances

2.1 Process and possibility of measuring

The complete mineralization of organic substances in water can generally be described by the following summation formula:

$$C_a H_b O_c + (a + \frac{b}{4} - \frac{c}{2}) \cdot O_2 = a \cdot CO_2 + \frac{b}{2} \cdot H_2O$$

From this it can be seen that the relation of

$$\frac{\text{degraded organic carbon}}{\text{resulting inorganic carbon}} = 1 \qquad (2)$$

or that

$$\frac{\Delta\ DOC}{\Delta\ CO_2} = \frac{12a}{44a} = \frac{3}{11} = \text{constant} \qquad (3)$$

3 g DOC must therefore be converted to 11 g CO_2 by mineralization, independent of the type of organic substances.

(Δ DOC = degraded dissolved organic carbon in g/m^3;
Δ CO_2 = increase of carbon dioxide in g/m^3)

Unfortunately, the analytical determination of small concentrations of carbon dioxide in water is difficult. If this analytical problem can be overcome, it will be possible to get exact data for the mineralized organic substances indirectly by CO_2 determination. On the other hand, it will also be necessary to determine the concentration of the dissolved organic carbon (DOC), which can be done very easily now by using the method of WÖLFEL and SONTHEIMER (1974).

Many kinds of analytical methods have been proposed for the determination of organics in water. Originally, the residue from burning at high temperatures was used to measure the organic substances because the reaction products carbon dioxide and water volatilize during complete combustion. However, the result is sometimes doubtful because of the other compounds in the water which may change during pyrolysis.

Later on, the oxidizability was measured with potassium permanganate. Even today there are analyses sheets containing the term "organic substance" instead of "oxidizability".

After several variations of oxidizability with potassium permanganate remained unsatisfactory, another oxidation agent is now being tried, namely potassium dichromate In wastewater technique, on the other hand, the determination of biological oxygen demand was used in order to be able to draw conclusions on the effect of purification steps.

More or less, it was always the aim to be able to draw conclusions on the amount of organic substances by measuring the oxygen required for their oxidation. That this is not possible is shown by the quotient (Q) of oxidizability (COD) and organic carbon (DOC) using the mineralization summation formula. Even at complete oxidation, which is difficult to achieve in most cases, the quotient can never be constant but is always depending on the type of organic substances:

$$Q = \frac{COD}{DOC} = \frac{2}{3} \frac{4a + b - 2c}{a} = \frac{2}{3} \left(4 + \frac{b - 2c}{a}\right) \qquad (4)$$

Therefore, the oxidizability should not be taken as a criterion for the total amount of organic carbon present in the water. Indeed, also in practice the relation is never constant (SONTHEIMER 1970). All the same, a continuous control of the oxidizability, in addition to the content of organic carbon, is of interest for the water quality, because conclusions can be drawn from the quotient on the nature of the organic substances.

If one wants to investigate the process taking place in a biologically operating activated carbon filter, the decrease of the dissolved organic carbon (Δ DOC) and the increase of inorganic carbon (Δ inorg. C) allows some important conclusions to be drawn, provided there is only mineralization and adsorption.

When Δ DOC $-$ Δ inorganic C. $= 0$ (5)

then there is only mineralization. If the decrease of the organic carbon content is higher than the increase of inorganic carbon, i.e. if

$$\Delta \text{ DOC} - \Delta \text{ inorganic C.} > 0 \qquad (6)$$

then adsorption is more important, the increase being more pronounced the bigger the positive deviation. In the opposite case, i.e. when

$$\Delta \text{ DOC} - \Delta \text{ inorg. C} < 0 \qquad (7)$$

then mineralization predominates, which means that primarily adsorbed substances are mineralized onto the activated carbon. A special case with strongly negative values, where inorganic substances are formed apparently without a decrease in organic substances, will be discussed in chapter 3.6.

2.2 The kinetics of mineralization

The mineralization process in activated carbon filters can be divided as follows:

1. Adsorption
2. Biochemical degradation

Here mineralization is slowest and thus a velocity-determining process.

When water which contains organic substances is treated in a fresh activated carbon filter bed there is, in fact, at first an adsorption. Only after some weeks (normally after two to three months) the biochemical processes of mineralization of organic substances are "in full swing". This breaking-in period is apparently typical for all biochemical processes because they are noticed on a similar scale also with the biological removal of manganese or with the nitrification of ammonia.

After the breaking-in period the adsorption and the biochemical degradation of organic substances take place in parallel, during which time either adsorption or mineralization may exceed for a time. Here the velocity of mineralization is constant and takes place in a steady manner, independent of of the concentration of organics in water, when conditions remain unchanged such as for instance temperature and filter bed loading. In the fully loaded activated carbon bed only that amount of organics can be newly adsorbed which has previously been removed by mineralization (see Chapter 3.8). Different situations arise when the concentrations in the raw water vary (see Chapter 3.7).

Our tests have shown that the following differential equation will be valid:

$$-\frac{d\ DOC}{dt} = k \qquad (8)$$

This differential equation, which has been confirmed by the results, leads to the following solution:

$$\Delta\ \mathrm{DOC} = \mathrm{DOC}_o - \mathrm{DOC} = k \cdot t \qquad (9)$$

If time t is replaced in this equation by

$$t = \frac{\varepsilon \cdot l_F}{v_F} \qquad (10)$$

then the following formula results for the specific biochemical filter degradation capacity:

$$N_F = k \cdot \xi = \Delta\ \mathrm{DOC} \cdot \frac{v_F}{l_F} \qquad (11)$$

Abbreviations:

DOC = concentration of dissolved organic carbon in g/m^3 after the carbon filter

DOC_o = dissolved organic carbon in g/m^3 in raw water

Δ DOC = decrease of dissolved organic carbon during filtration

l_F = filter length in m

ν_F = filter velocity in m/h

ε = relation of the water volume to the total volume of the filter bed

N_F = specific biochemical filter degradation effectiveness per m^3 of filter bed volume in g DOC/m^3 per hour

Further parameters of the filter effectiveness are temperature, activated carbon material, size of granules and type of organic substance. The influence of these parameters on the filter performance could not be defined in more detail, because they did not remain constant during the practical tests. It can be said, however, that the biochemical degradation effectiveness N_F increases with increasing temperature, with the decrease in size of the activated carbon granules and with an improved adsorption capacity as well as with larger conducting pores of the activated carbon. It can be assumed that the degradation efficiency is better when the substances in the water are more easily biodegradable.

The degradation efficiency N_F achieved in the tests was in the range of 1 to 4 g DOC per m^3 activated carbon per hour.

3. Experience with the use of biologically effective activated carbon

3.1 Experience gained with the common technology

The purpose of using activated carbon filters in water treatment has always been the removal of undesired substances from the water by adsorption. For a long time the main field of using activated carbon filters was chiefly dechlorination.

At the beginning of the 1960s activated carbon was used with success for the removal of taste and odour at the lower Rhine-river. Here it was possible to overcome the problems of steadily deteriorating quality of the surface waters (HOPF 1960). The present state of process techniques is described in detail in the other papers.

Already when using granular activated carbon as filter material for dechlorination in the beverage industry,it was noticed that even with high concentrations of chlorine of about 5 g/m^3 in the raw water, it was not possible to avoid germ formation. Only by subjecting the filter material to hot steam disinfection every week, it was possible to solve this problem. However, this method was not practicable in waterworks because of the large filter sizes. Even the use of extremely high chlorine concentrations brought about no improvement (ROGGENKAMP 1968).

It is known that this observation of bacterial growth in the beverage industry slowed the wider use of activated carbon filters. On the other hand, this effect did not occur with the filters along the river Rhine. There is no explanation so far for this different behaviour.

3.2 Microbiological degradation of persistent organic substances using activated carbon

It was proved by laboratory tests that activated carbon can improve biological degradation, because the biochemical degradation of formic acid can be accelerated by the presence of activated carbon. Furthermore, it was possible to prove experimentally in the laboratory that normally persistent pentaerythritol mineralizes completely in the presence of granular activated carbon after a certain introductory period of 60 days (KOPPE et al 1974). This is not surprising when one remembers that activated carbon adsorbs organic substances by accumulating it at the surface and that there seems to be no clearly defined boundary between biodegradability and persistency.

It seems to be a question of time rather, and perhaps also of biological adaption, to decide on the degradation and persistency. So, if it becomes possible to fix, with the aid of activated carbon, organics which are difficult to degrade for a sufficiently long time in order to subject them to a decomposition process long enough, then the limitations of biological degradation in wastewater treatment will be eased too. This could lead to a considerable success in wastewater purification and to a better water quality of our surface waters (RINKE et al 1975).

3.3 Pretreatment of the water before filtration

The presumption that the pretreatment of the water before activated carbon filtration has a great influence was clearly confirmed by the tests made in Bremen. Consequently, a pre-chlorination proved to be adverse in every way.

This was true regarding the high colony numbers of the filtrate and the low removal efficiency of organic substances. According to our observations, we feel that some unfortunate experience in connection with activated carbon filters in the past was due to the fact that prechlorination was used. If one avoids this pretreatment, much better results will be obtained.

After an unused activated carbon filter has been put into operation, a normal biological development occurs in the filter bed, as we know it from slow sand filters (HUSMANN 1958), SCHMIDT 1963). This has been noticed with the test filters in Bremen too, and could not be expected to be otherwise because the supply of nutrients is high, and the activated carbon adsorbs the organics contained in the water and stores them in its pores. Therefore, the mineralizing bacteria have an extremely large supply of nutrients at their disposal. These bacteria may be compared with a herd of cows grazing in a juicy and luscious meadow. It is also known that this activated-carbon "meadow" is very spacious and rich in pores because of its large specific surface, providing ample room for many mineralizing bacteria, provided the pore structure will be suitable.

This biochemical mineralization is obviously disturbed decisively by pre-chlorination, the degree of the disturbance depending on the chlorine concentration before the filtration. The reason may be that chlorinated organic substances, formed through chlorination,are less biodegradable. According to our measurements, a pre-chlorination impairs the effect of activated carbon filtration to such an extent that this type of pretreatment ought not to be used in future. This is also true regarding sewage treatment.

On the other hand, one can be sure that the negative effect of chlorine does not depend on its oxidation ability. Therefore, preoxidation with potassium permanganate does not disturb the biological activity of carbon filters, while a pre-ozonization, using up to 5 g/m^3 of ozone, improves the effectiveness of the subsequent biological treatment step considerably (EBERHARDT et al 1974).

This improved biodegradability is due to the fact that some organic substances are transformed by ozone to a lower molecular weight. By this change they may become less adsorbable but more easily biodegradable. The ozone attacks especially at the double bonds of the organic substances and it may even remove organo chlorine from a molecule (GILBERT 1974). This may be another reason for the improved biodegradability. Incidentally, the same effect can be obtained by Gamma radiation (GILBERT 1974). The combination of ozone treatment with activated carbon filters in sequence is now a common water treatment process at the Lower Rhine (SIMON et al 1968). However, perhaps with the high filtration velocities there will not be enough time to get the full advantage of biological degradation within the activated carbon filter.

3.4 Hygienic problems with activated carbon filters

It cannot be expected that the effluent of a biologically operating activated carbon filter, with a filter velocity of 10 m/h, does not have any bacteria. . Similarly, this is not possible with slow sand filters whose filter velocity is 100 times lower. Measurements have shown that there will be a 90 % reduction in bacteria and coliforms with a biological activated carbon filter. In some cases there may be higher values, especially after a change in temperature and an adaptation of the micro-organisms to the new conditions. This is also true for slow sand filtration. Ozonization can also lead to higher numbers after a longer development period.

It will be worth-while therefore to consider an additional treatment step after a biofiltration to reduce the counts Slow sand filters with higher velocities (SCHALEKAMP 1971) or a low-dose chlorination may be advantageous. Only if there is an extensive reduction of organic substances within the carbon filter will there be a satisfactory disinfecting efficiency. In that case, subsequent chlorination or slow sand filtration will provide better safety and guarantee an excellent drinking water. Any additional removal of organic substances by the slow sand filter will not be possible, normally.

3.5 Removal of ammonia

Whilst the ammonium-ion in the usual concentration in natural waters has no toxic effects, difficulties may arise in the distribution system in the presence of ammonia (MADSEN 1975). It will be necessary therefore to remove ammonia when treating surface water. This is possible by biochemical nitrification in rapid sand filters, if the temperatures are higher than 5 °C. It is only necessary to ensure that there is enough oxygen in the water. Special means have to be taken if the NH_4-concentration exceeds 1.5 to 2 g/m^3.

Our tests have shown that nitrification in activated carbon filters has at least the same rate as in rapid sand filters. On the other hand, one cannot expect better results as ammonia cannot be adsorbed onto activated carbon. There is some significance in the test results in that carbon filters may have better efficiencies at low temperatures compared with rapid sand filters.

As usually it needs 3 months to start nitrification of ammonia, difficulties may arise with a sudden increase of the concentration in the surface water. In such a case it may be worthwhile to dose a small amount of ammonium salts to restore the biological activity. According to the results obtained from the pilot plant, this produces better efficiencies also for a temperature decrease below 50 °C.

It can be expected that the larger surface and increased pore volume of activated carbons will present some advantages of this filter material compared with other filters. Nitrifying bacteria may have more surface and space available. This may be the reason for the better efficiency at low temperatures.

3.6 Recycling of filtered water

During pilot plant tests the question arose if it might be possible to get a further reduction of the dissolved organic substances by recycling the treated water through the same filter. So a recycling test was made in which the removal of CO_2 and the enrichment in oxygen was achieved in a falling spray tower (EBERHARDT 1973). However, the assumption that, after several cycles, the water would be free from dissolved organics was not confirmed in any way. It was observed that during the recycling the DOC values even increased at first, after which it took some time until they regained the original value of the normal throughput. On the other hand, mineralization still took place, as could be seen from the enrichment in CO_2 and the decrease in oxygen after each passage through the filter. These values remained constant for several weeks. This leads to the conclusion that the adsorbed organic substances will be biodegraded and mineralized by recycling, as long as there is sufficient oxygen for the reaction and as long as the produced CO_2 is removed. There was no large influence of the concentrations of O_2 and CO_2 on the mineralization rate.

These observations prove that adsorption precedes mineralization in a biological activated carbon filter. They show further that the rate of mineralization is of zero order and that it does depend on the amount of loaded carbon and time only. This means that there are steady-state conditions for this process and a given filter.

3.7 Buffer effect of activated carbon filters.

Already during the initial stages of the pilot plant tests, it was observed that the treated water from the carbon filter had a more uniform quality than the filtrate from the slow sand filters. The tests described above now explain why it was possible to get a more constant water quality from the carbon filters. Here we have a buffer effect through the combination of adsorption and mineralization taking place at the same time. Whilst there is almost no adsorption capacity in slow sand filters, an increase in raw water quality will also lead to an increase in the treated water. This is not the case with activated carbon filters where higher concentrations in the raw water change the equilibrium data, so that higher loadings will occur and a better removal efficiency. On the other hand, with lower concentrations of raw water there may also be desorption, and these two effects will lead to a more uniform effluent of a biological carbon filter, which may have some advantage.

3.8 Biological regeneration of activated carbon

As the mineralization of the organic substances adsorbed onto the carbon is independent of the raw water concentration, a stopping of the filter flow may lead to oxygen deficiency in the filter and to changes in water quality through anaerobic conditions. To avoid this, such carbon filters must have a steady water flow. However, this is no disadvantage as one might assume when regarding the costs for pumping. This is due to the fact that it will be possible to do biological regeneration of the carbon also at times when low water quantities are needed and makes it possible to use higher velocities when maximum capacity is necessary. In this way, biological regeneration is also possible during recycling times.

Bearing this in mind, it may be said that biological carbon filters differ from the usual adsorption plants by the fact that apart from normal adsorption there is also a biological regeneration of the activated carbon in use. From the pilot plant data it cannot be said whether a total regeneration of a carbon will be possible with this technique, because regeneration would need several years. Such a long period is not very attractive from a practical point of view.

But, in any case, biological regeneration will aid a longer running time also in those cases where only normal adsorption is needed; it will also mean better economics of activated carbon filters. It will merely be necessary to have optimum conditions for biological mineralization.

4. Design of biofilters using activated carbon

The design of a biological activated carbon filter can be made by using the following formula:

$$l_F = \frac{\Delta\ DOC \cdot v_F}{N_F} \qquad (13)$$

Δ DOC = reduction of DOC concentration by the filter (g/m^3)

v_F = filter velocity (m/h)

l_F = length of filter (m)

N_F = specific filter efficiency (g/m^3 per hour)

A value for N_F of 1 g DOC/m^3/h may be generally regarded as conservative.

Assumed example:

$$\begin{aligned} \text{DOC of raw water} &= 4\ g/m^3 \\ \text{DOC of treated water} &= 1\ g/m^3 \\ \Delta\ \text{DOC} &= 3\ g/m^3 \end{aligned}$$

These data lead to different filter velocities:

$$v_F = 10\ m/h \quad l_F = \frac{3 \cdot 10}{1} = 30\ m$$

$$v_F = 3\ m/h \quad l_F = \frac{3 \cdot 3}{1} = 9\ m$$

If the 9 m are divided into two units, having a spray in between (see Fig. 1), useful results and a satisfactory treatment can be achieved. This plant also permits recycling without any particular problems, and this type of treatment is especially advantageous during high temperatures in the summer, when it provides the only means to avoid anaerobic conditions. Similar results can be obtained by a so-called dry filtration. However, care must be taken as mechanical deterioration of the carbon granules may be of some influence.

Fig. 1

The calculated filter velocity of 3 m/h seems low if compared with rapid sand filtration. However, it should be remembered that a reduction from 4 to 1 g/m^3 of DOC needs a high biological activity. Slow sand filters normally need a filter area which is 50 to 100 times larger. In the tests the specific efficiency of slow sand filters was calculated as

$$N_F = 0.02\ g\ DOC/m^3\ sand \cdot hour$$

From this figure it cannot be concluded that the same rules apply to slow sand filters and to activated carbon filters; however, a comparison may be made with the 1 to 4 $g/m^3 \cdot h$ DOC.

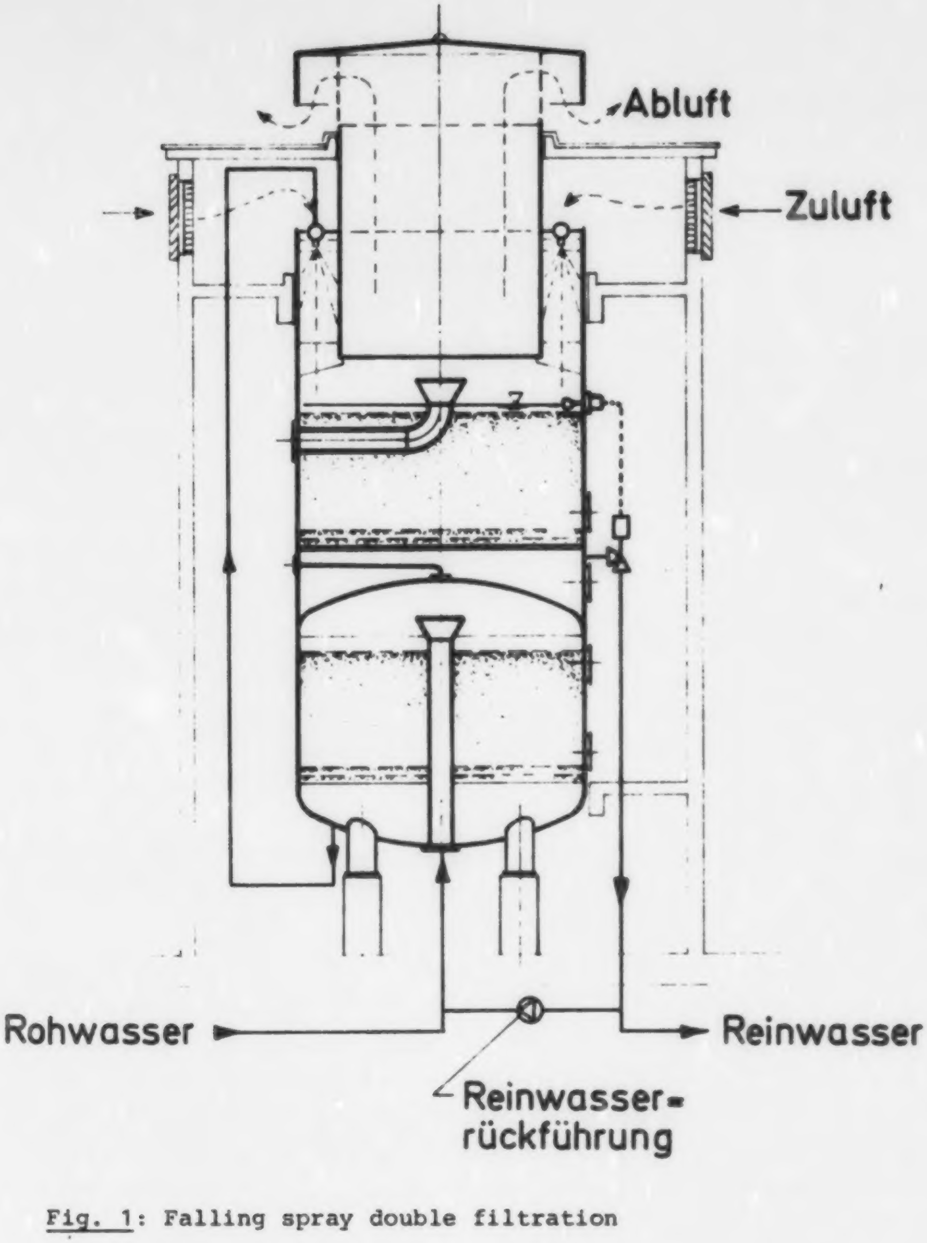

Abluft
Zuluft
Rohwasser
Reinwasser
Reinwasser-rückführung

Fig. 1: Falling spray double filtration

Abluft: used air
Zuluft: fresh air
Reinwasser: treated water
Reinwasserrückführung: recycling of treated water
Rohwasser: raw water

5. Final remarks

Starting with some theoretical considerations, this report presents a review of the results of the work at a pilot plant over several years. The effectiveness of biological activated carbon filters can be compared with that of slow sand filters regarding the biological processes. The difference lies in the reaction rate which is 10 to 100 times higher per volume in a carbon filter. This depends on the high concentration of organics in the pores of the activated carbon, and on the fact that the process starts with adsorption, after which biological mineralization and regeneration takes place. This mechanism may be the reason that a degradation of normally persistent substances can also be observed. For practical use, the buffer capacity of such a system is of importance too.

Investigations of the mineralization rate have shown that a zero reaction order can be used to describe the process kinetics, which leads to a very simple design formula. However, before adopting it, it should be checked whether these results can be confirmed by other waterworks, because the water used for these tests has undergone a very intensive pretreatment.

Some investigations into the presence and behaviour of bacteria in activated carbon filters

by D. van der Kooij, Netherlands

Introduction

The application of activated carbon filtration in tapwater preparation is based on the adsorptive action of the carbon by which organic substances like organochlorine compounds, taste and odour compounds and many organics originating from industrial waste, can be removed from the raw water. Also biological processes affect the quality of the water flowing through the filter. These biological processes are mainly caused by the bacteria which oxidized biodegradable organic substances and ammonia. However, this bacteriological activity in the carbonfilters takes up oxygen from the water and also results in the presence of large numbers of bacteria in the filtrate (Bernard 1970, Ford 1973 Wallis et al 1974).
It is generally assumed that the bacteriological activity in carbon filters is intensified by the adsorption of organic substances (Sontheimer, 1974 and Eberhardt et al., 1974) and that bacterial activity in carbon filters results in a increase of the adsorption capacity (Eberhardt et al, 1974).
Much attention is paid to the application of carbon filtration in drinking water preparation processes in The Netherlands. As an increased amount of drinking water must be prepared from surface water of a steadily decreasing quality. Investigations were therefore carried out into biological and physicochemical processes in carbon filters at the Testing and Research Institute of the Dutch Waterworks KIWA N.V.. Some experiments with the bacteriological behaviour in carbon filters are described in this paper.

Experiments and results

The influence of the kind of filtermaterial on the development of bacteria in the filterbed was investigated in three experimental filters. These filters contained granulated activated carbon Norit ROW 0,8 Supra; non activated (n.a.) carbon (Norit ROW 0,8); sand (0,85-1,00 mm) respectively. The filters were fed with tapwater (13 °C-17 °C) (superficial contact time and velocity: 3 minutes and 3,5 m/hr) during 10 months respectively. Bacterial numbers on the filtermaterials were estimated at regular intervals by the colony count technique on a diluted nutrient agar (0,35 gl^{-1} beef-extract; 0,65 gl^{-1} peptone and agar: 10 gl^{-1}) after incubation at 25 °C during 10 days. The numbers of bacteria on the filtering materials were expressed in number per ml filtervolume. The results of the experiments are shown in Figure 1.

▲ activated carbon Norit ROW 0,8 Supra
△ non activated carbon Norit ROW 0,8
○ sand (0,85 - 1,00 mm)

Bacterial numbers on activated carbon ROW 0,8 Supra ROW 0,8 (non activated) and sand (0,85 - 1,00 mm) when fed with tapwater (Superficial velocity 3,5 m/hr).

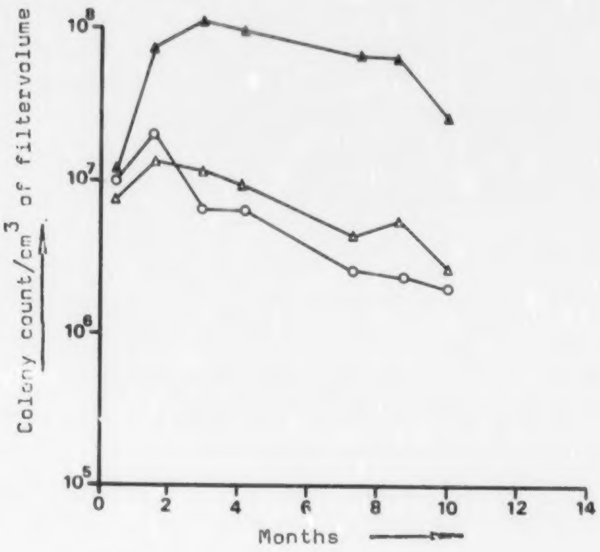
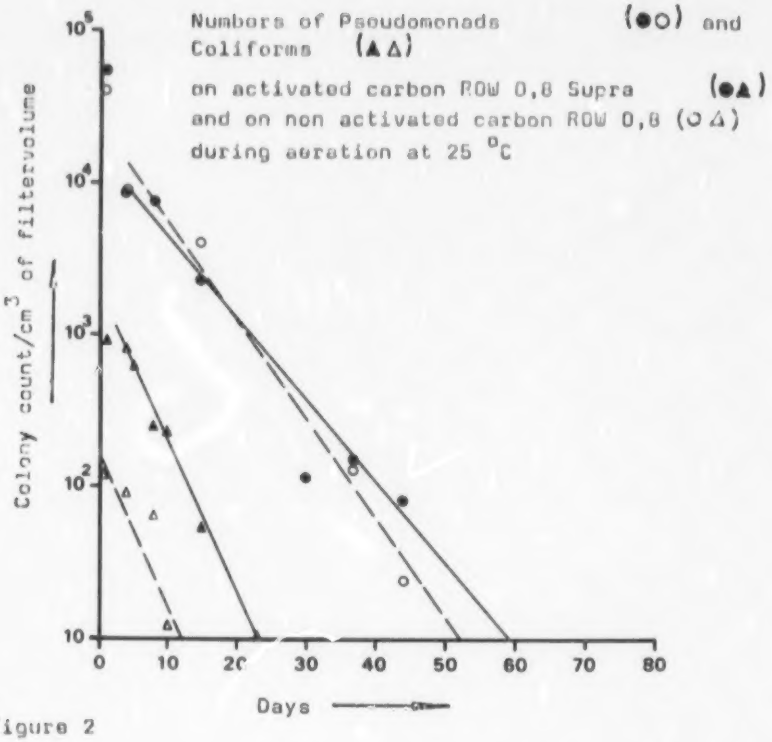


FIGURE 1

Another experiment was carried out with samples of activated carbon ROW 0,8 Supra and the non activated carbon ROW 0,8 (n.a.) taken from filters which had been fed with prefiltered river water during one year. The wet carbon samples of 150 ml were supplied with 50 ml of tapwater and aerated at 25 °C. The numbers of Coliforms, Pseudomonads and Actinomycetes on the carbons were estimated weekly by selective media. The total number of viable bacteria was estimated by the colony count on the diluted nutrient agar. All counts were expressed in number per cm^3 filter volume. The oxygen consumption of the carbons was estimated with a Y.S.I. Oxygen Monitor and expressed in mg O_2 liter filter volume per hour.
The results of the experiments are shown in Figs. 2 and 3.
Table 1 shows the 50 % reduction times of the bacteria on the activated carbon and on the non activated carbon.

Discussion and conclusions

It is shown in Figure 1 that the numbers of bacteria on the activated carbon were always about ten times higher than the numbers of bacteria on the non activated carbon and the sand. The surface area at the disposal of one bacterial cell can be calculated from the colony count and the hypothetical surface area of the cylindrical carbon particles. The hypothetical cylindrical surface area of the granulated activated carbon is about 40 cm^2/cm^3 and when the colony count is $10^8/cm^3$ 40 μ^2 of this surface will be at the disposal of one bacterial cell. The real surface area of the activated carbon particles however, is much larger than 40 cm^2/cm^3. This causes a very low density of bacteria on the surface of the activated carbon, even when it is realized that the colony count is only a small minority of the bacteria present on the particles. Observations with an electron-scan microscope confirmed this conclusion and it is reasonable therefore to state that adsorption processes are not hindered by the presence of the bacteria on the carbon.
It is shown in Figure 1 that the number of bacteria on the activated carbon is decreasing after having reached its maximum. It can be concluded that this decrease is not caused by exhaustion of the adsorptive capacity of the activated carbon since this phenomenon was also observed with the non activated carbon and the sand. The decline in bacterial numbers might be explained by the occurrence of a shift in the composition of the bacterial flora towards bacteria which do not participate in the colony counts.
The results of the aeration experiments are shown in Figs. 2 and 3 and in Table 1. The numbers of both the Coliforms and Pseudomonads and total colony forming bacteria decreased on the activated as well as on the non activated carbon (Fig. 2).



Numbers of Pseudomonads (●○) and Coliforms (▲△)
on activated carbon ROW 0,8 Supra (●▲)
and on non activated carbon ROW 0,8 (○△)
during aeration at 25 °C

Figure 2

Numbers of bacteria (colony forming units) (▲△) and
numbers of Actinomycetes (●○)
on activated carbon ROW 0,8 Supra (▲●)
and non activated ROW 0,8 (△○) during aeration at 25 °C
o——o oxygen consumption (mg O_2 l^{-1} hr^{-1}) ROW 0,8 Supra
o- - - -o " " " " " ROW 0,8 (n.a.)

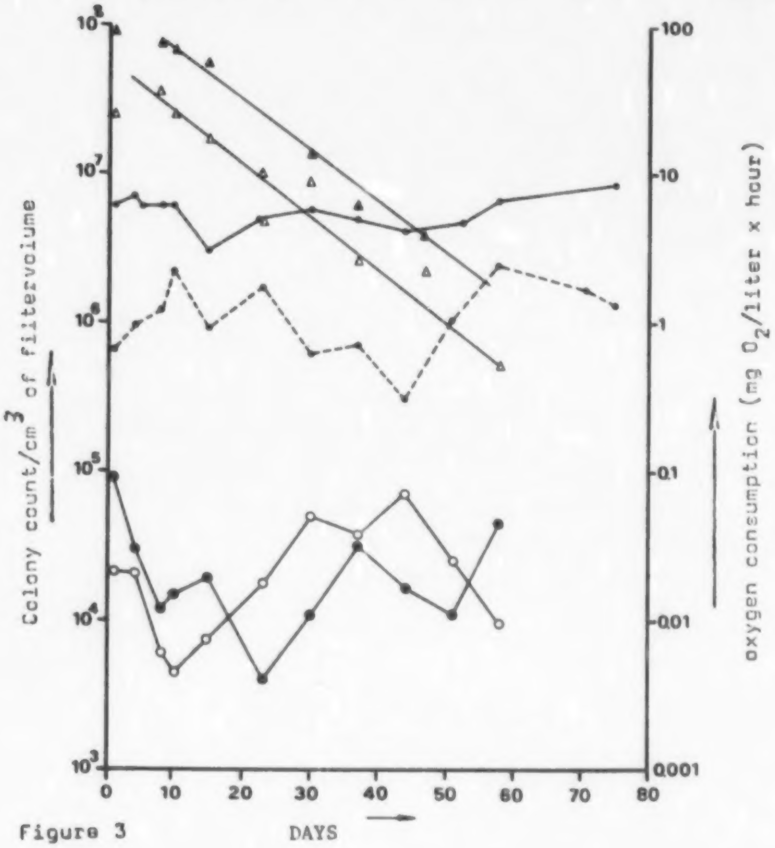


Figure 3

Table 1

50 % REDUCTION TIMES (DAYS) OF DIFFERENT GROUPS OF BACTERIA ON ROW 0,8 SUPRA AND ROW 0,8 N.A.

Type of bacteria	ROW 0,8 Supra	ROW 08 n.a.
Colony forming units(25 °C, 10 days)	9	8,5
Coliforms	3	3,5
Pseudomonads	4,5	4,0
Actinomycetes	>50	>50

However, the numbers of Actinomycetes and the oxygen consumption did not show a clear decrease within a 60 days period (Fig. 3). The 50 % reduction times of the different groups of bacteria are shown in Table 1. From this table appears that Coliforms disappear quicker than all other bacteria. There is hardly any difference between the 50 % reduction times of the selected groups of bacteria on the activated carbon and the ones on the non activated carbon. It is therefore concluded that neither Coliforms nor Pseudomonads nor the total colony forming bacteria had any advantage of the organic substances which must be present on the activated carbon after having been in contact with riverwater for one year. This conclusion is in contrast with the general assumption that bacteria present in activated carbonfilters are able to utilize adsorbed organic substances. (Sontheimer 1974, Eberhardt et al 1975).

The oxygen consumption of the activated and non activated carbons did not decrease with the decreasing colony counts. Nor did the numbers of Actinomycetes but these low numbers (Fig. 3) can not be held responsible for the oxygen consumption. It is possible therefore that the oxygen consumption of both types of carbon is caused by chemical rather than by bacteriological processes. The fact that the Actinomycetes showed decrease within 60 days might be due to their ability of producing spores.

The influence of dissolved organic compounds on flocculation

by G. Albert

Introduction

In water treatment flocculation is often brought about by the addition of hydrolyzing metal salts. Generally, these salts give greater reduction in turbidity, and in addition one obtains some degree of removal of dissolved organic compounds. Thus these unwanted substances can be partially removed simply and economically while at the same time reducing loading on subsequent polishing steps, e.g. with activated carbon. It is desirable therefore to make the flocculation conditions such that both colloidal and dissolved organic compounds are removed together as far as possible. In order to achieve this aim the fundamental mechanisms of sorption of organic compounds to flocs and of agglomeration or colloidal material have to be understood.

Theoretical considerations

A considerable amount of work has been published concerning the effect of various factors on flocculation processes in water treatment. PACKHAM (1963) has completed an extensive review on the use of metal salts as flocculants. Additional information can be obtained from later reviews such as has been made by the COMMITTEE REPORT (1971) and also by O'MELIA (1972). STUMM (1967) has discussed the different mechanisms responsible for flocculation by adding hydrolyzing metal salts. Due to the hydrolytic reaction of metal ion and the water, various hydrolysis products are formed which are able to destabilize colloids in different ways. The metal ions are hydrated in water as aquo-complexes such as $Al(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$ which are present at low pH values. The hydrolytic reactions of iron are similar to those of aluminum so that only aluminum is considered in detail. With increasing pH, the loss of hydrogen ions leads to the formation of $Al(H_2O)_5\ OH^{2+}$, then to the formation of $Al(H_2O)_4\ (OH)_2^{+}$ and the uncharged aluminum hydroxide $Al(H_2O)_3(OH)_3$ which shows only a low solubility. With higher pH the highly soluble complex $Al(H_2O)_2(OH)_4^-$ is present. Besides these species also polymeric hydroxo metal complexes are formed. A number of such complexes are known containing varying ratios of metal ion to hydroxyl groups between 1:2,5 and 1:3. Distribution diagrams for the different Al- and Fe(III)-species, calculated from the corresponding thermodynamics equilibrium constants, are given by O'MELIA (1972) and STUMM (1967). According to the equilibria, polymeric species are found at pH-values between 4 and 6. They are very effective in destabilizing negatively charged colloids becuase of their strong tendency to be adsorbed at interfaces (STUMM and HAHN, 1967). At very low colloid concentration this destabilizing ability is ineffective because of the low collision efficiency. In such systems agglomeration of colloidal particles takes place predominantly by coprecipitation; the particles are enmeshed in the precipitating aluminum or ferric hydroxides. Consequently optimum flocculation conditions are found near neutral pH where hydroxide is formed. This mechanism has been confirmed by PACKHAM (1965) who studied the coagulation of various dilute colloidal systems.

The first studies on the removal of organic compounds by flocculation were reported by BLACK, SINGLEY et al in 1963 where the importance of chemical mechanisms was affirmed. HALL and PACKHAM (1963) examined the removal of humic acids and proposed a purely chemical precipitation of basic iron or aluminum huminates. According to STUMM and MORGAN (1962) complex formation reactions between aluminum and iron coagulant metal ions and carboxylic, phosphate, sulfate and aromatic hydroxy functional groups are important in the elimination of dissolved compounds. Therefore, the pH should play a predominant role in this process. SCHILLING (1975), however, found that pH did not have a marked effect on the removal of humic acids.

The precipitation of dissolved organic compounds may cause additional turbidity. On the other hand, a large number of natural organic compounds are of high molecular weight. Therefore it can be expected that they act also as flocculant used in water treatment. In this case the flocculation of colloidal material may be improved by the presence of organic compounds.

In this study several typical organic compounds are evaluated on their influence on turbidity removal.

Experimental

All experiments were carried out using a standard jar test in 1 l-beaker in a constant temperature bath at 25°C. After the flocculant was added, the suspensions were stirred for one minute at 150 rpm, then for 30 minutes at 50 rpm. After a sedimentation time of one hour a sample was taken from the supernatant in order to measure turbidity, pH and residual amount of flocculant and of organic matter.

The turbidity was determined in a Hach 2100 A turbidity meter. The measured values were related to the values which were obtained without flocculant addition at the sampe pH and amount of mixing.

The residual amount of flocculant was analyzed by standard analytical techniques. Organic compounds which may interfere with the analysis were removed by oxidation using an ultraviolet radiation technique (WOLFEL, SONTHEIMER, 1974).

The residual amount of organic substances was determined photometrically, or if this method failed by DOC-measurements. Unless noted otherwise, analytical grade chemicals were used. pH was varied by adding HCl or NaOH before the addition of flocculant. Both tap water (total hardness: 3,5 mg/ℓ) and deionized water was used.

Quartz powder was selected as a typical turbid component in surface water The powder used, from the Quarzwerke, Cologne, had a specific surface of 4 m^2/g (BET) and a size distribution between 1 and 10 μm. A suspension of 100 ppm SiO_2 corresponds to a turbidity of nearly 20 JTU at neutral pH in deionized water.

Results

As is seen in Fig. 1, the maximum removal of quartz particles occurs in a pH range where $Al(OH)_3$ or $Fe(OH)_3$ are present. It appears therefore that the quartz particles are flocculated by enmeshment in metal hydroxide. There are similar conditions to those found by PACKHAM (1962). Both curves for iron and aluminum are nearly identical. The flocculation region is extended if additional ions are present as can be seen by the results which were obtained with tap water.

When an organic component, which does not react with aluminum to form an insoluble complex, is present, no influence on flocculation - as is seen from turbidity removal - can be detected. Also no removal of organics takes place as can be seen from Fig. 2. There 0.111 mmol Al/l was added to 0.06 mmol vanillic acid. There are selected similar conditions for flocculant concentration and dissolved organic carbon values to those generally obtained where treating drinking water.

As is known, many dyes form insoluble complexes with multivalent cations. Congo red, which was selected for this study, can be precipitated completely by the addition of aluminum sulfate as is shown in Fig. 3. A ratio of 5.5 of aluminum to congo red equivalents was used, which corresponds to the conditions in Fig. 2. Because the percentage of trivalent aluminum ions, which reacts with the dye, decreases with increasing pH due to hydrolysis, precipitation occurs only in the acid region. The reduction in turbidity takes place in the same region as the precipitation of organic substances. This indicates that the quartz particles are removed by coprecipitation with the dye complex, since $Al(OH)_3$ flocs are not formed at this pH. It is possible that flocculation takes place by a similar mechanism to polyacrylic acid flocculants where, according to VOLLMERT and SONTHEIMER (1973) colloidal particles are enmeshed in the network of crosslinked polymers.

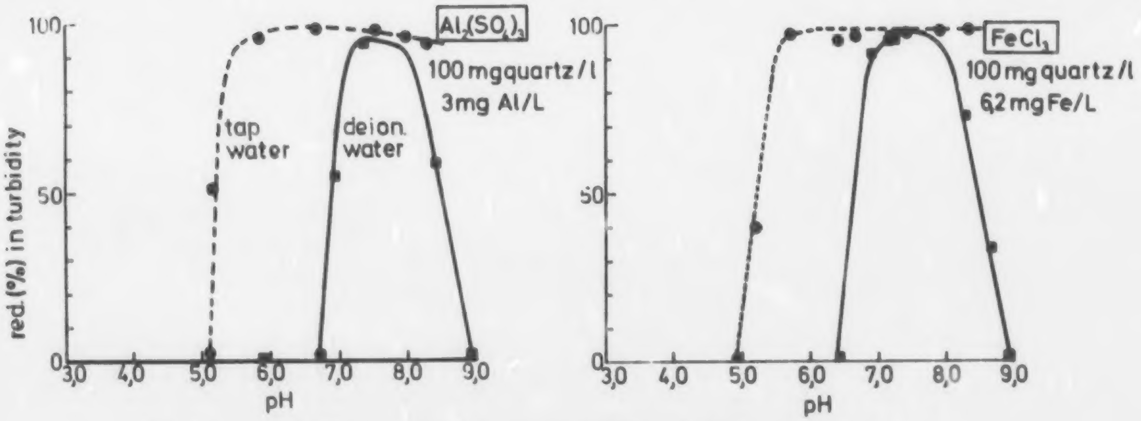


Fig. 1 Turbidity removal by iron (III) and aluminum salts
100 ppm SiO_2/ℓ, 0.111 mmol Al and Fe/ℓ

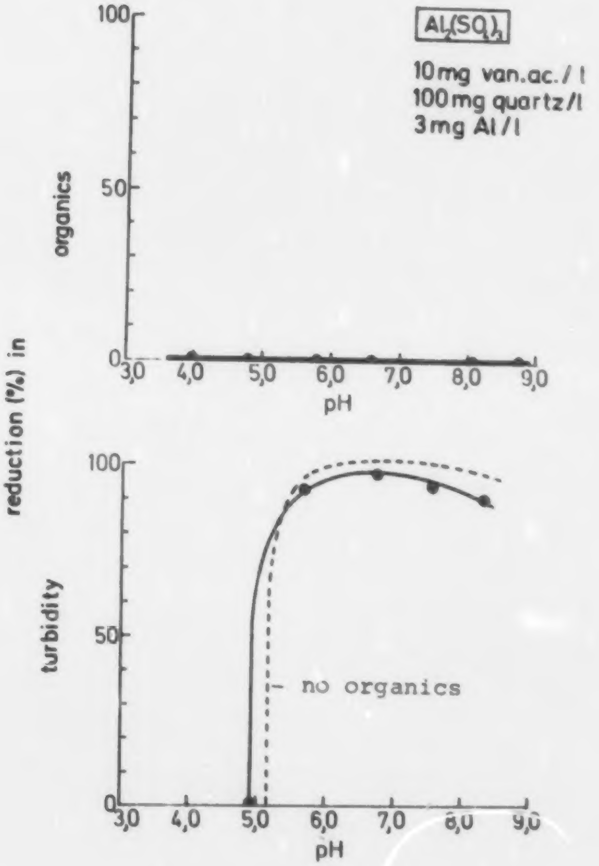


Fig. 2 Elimination of vanillic acid
10 ppm vanillic acid
0.111 mmol Al/l
100 ppm SiO_2, tap water

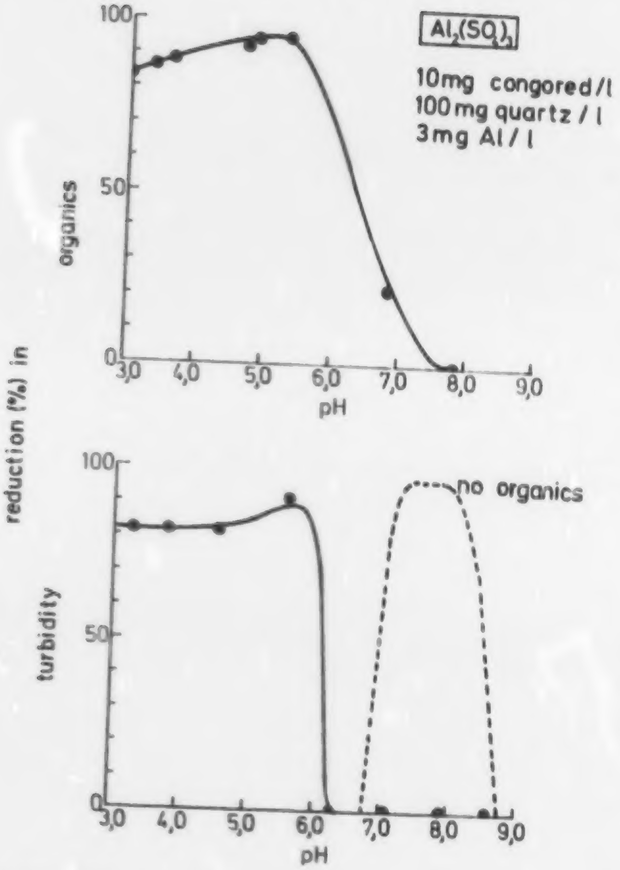


Fig. 3 Elimination of congo red
10 ppm congo red
0,05 mmol Al/1
100 ppm SiO_2/1, deionized water

Lignin sulfonic acid, a typical waste product of paper mills, acts in a similar way. A commercially available product from Roth, Germany, was used for these experiments. The acid number, which was determined according to a method developed by MAIER (1975) amounts to 2.5 acid equivalents per gram organic matter. As shown in Fig. 4, a sixfold excess of metal ions precipitated only 75 percent of the organic matter, the other 25 percent remaining dissolved. The relatively sharp optimum for the removal of organic material and for the turbidity reduction is due to the fact that only the dissociated acid can react with the trivalent metal ion to form the insoluble complex. The percentage of trivalent aluminum decreases but the dissociation of the acid increases with increasing pH. The combination of these two equilibria produces such an optimum. The precipitation occurs at lower pH values because less hydroxyl groups are needed to neutralize the aluminum ions. The precipitation by ferric chloride occurs at a lower pH than aluminum sulfate due to the different hydrolysis constants, as can be seen from the distribution diagrams for the two metal ions. A more extended optimum is obtained by using Polyaluminum chloride (PAC) as a flocculant. This relatively new flocculant was obtained from SACHTLEBEN AG, Duisburg. Another typical water pollutant but of natural origin is humic acid. The used humic acid was extracted from the Lake of Constance. The water was filtered through a macroporous anion exchanger. By regeneration of the resin with sodium hydroxide the sodium huminate was obtained which was converted in the hydrogen form by a cation exchanger. After evaporation the solid residue was washed with ethanol for several times until the salt content fell below 3%. The product obtained was found to be mainly humic acid. Nearly 85% of the substance could be precipitated by iron- or aluminum salts. It had an acid number of 8.1 acid equivalents per gram. The results shown in Fig. 5 were obtained by adding a 5.5 fold excess of equivalent metal ions. There are some characteristic differences between the three flocculants used. Contrary to aluminum sulfate ferric chloride produces a precipitate with humic acid, where the quartz particles could be enmeshed. Under the given concentration one can distinguish two zones. At low pH quartz particles are enmeshed in

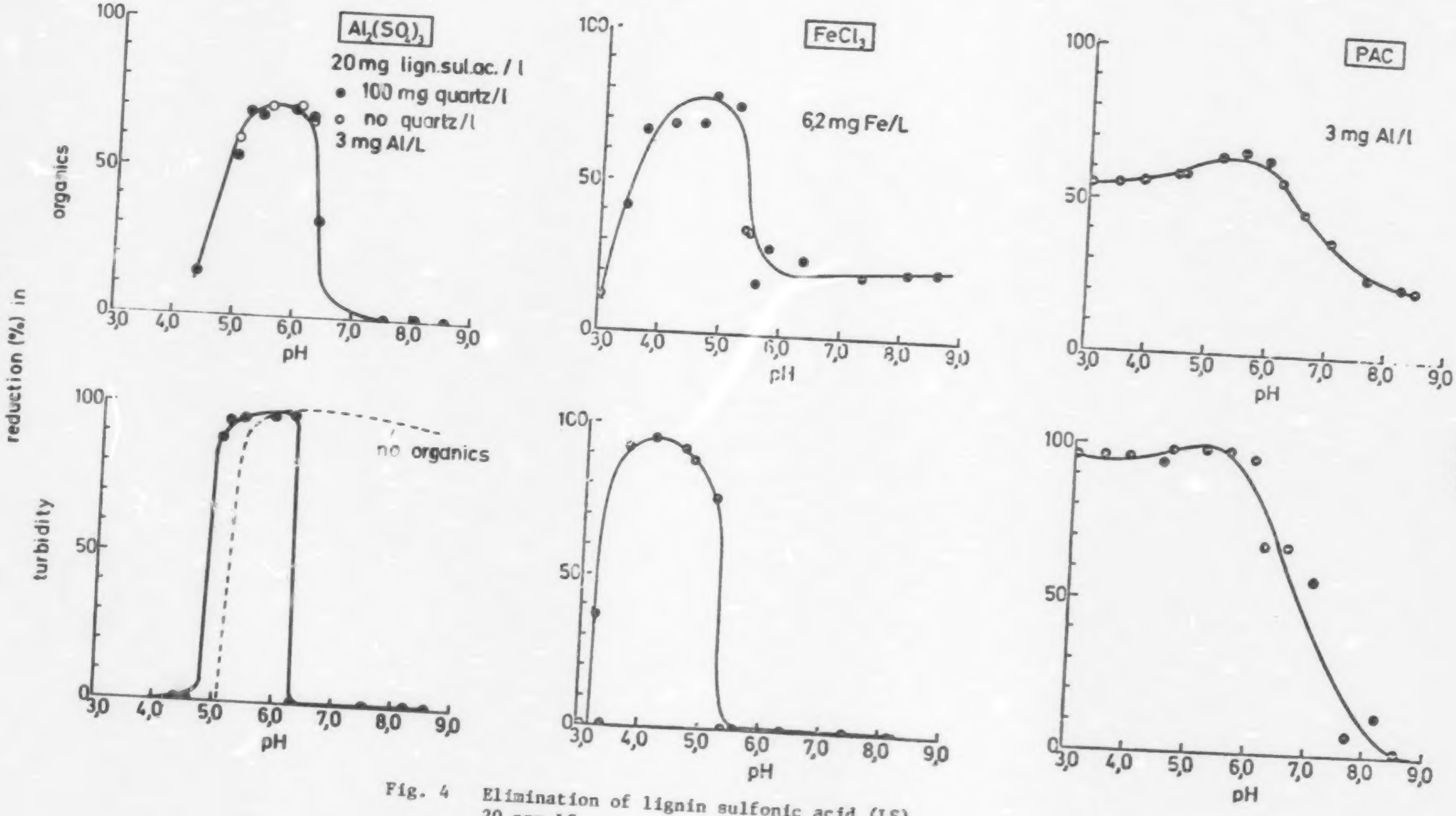


Fig. 4 Elimination of lignin sulfonic acid (LS)
20 ppm LS
0.111 mmol Al and Fe/l
100 ppm SiO_2/1, tap water

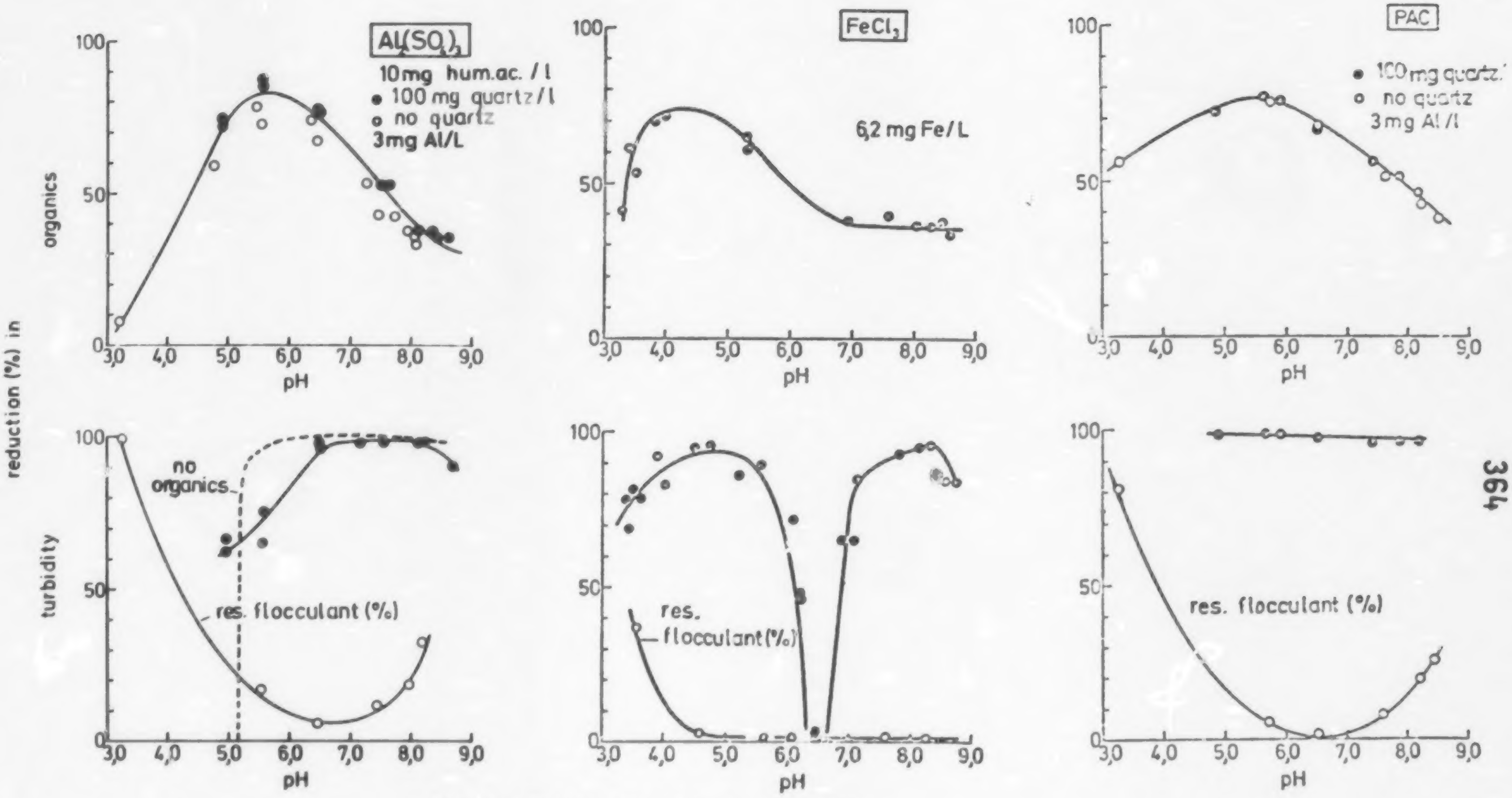


Fig. 5 Elimination of humic acid (HS)
10 ppm HS
0.111 mmol Al and Fe/ℓ
100 ppm SiO_2/l, tap water

the precipitate of ferric huminate; aluminum huminate causing only additional turbidity. Near the neutral pH one observes coprecipitation by $Al(OH)_3$ or $Fe(OH)_3$. The optimum of reduction in humic acid occurs at lower pH for ferric chloride than aluminum sulfate or PAC. However, PAC gave turbidity removal over a large pH range.

No marked influence of anions could be observed. $AlCl_3$ and $Al_2(SO_4)$ produced the same results (Fig. 6).

Also, neither the method of addition of the flocculant nor the way of mixing influenced the removal of organic substances. In Fig. 7 the results of experiments are shown where the speed of adding the floculant was varied.

When the precipitate was always removed and a new portion of flocculant was added to the supernatant, the same result was obtained when the whole portion was added. It indicates too that only chemical reactions are responsible for reduction in organics. The nonlinear curve for humic acid in Fig. 8 may be due to the range of acids present, or it may be caused by a distribution in the molecular weight of the acid.

Differences could be detected if the organic matter was added after the flocculant. The anions of the humic acid are replaced by the hydroxyl ions so that the removal of humic acid decreases with increasing age of the aluminum hydroxide floc (Fig. 9).

The optimum pH of removal depends on the ratio of humic acid present in solution. Increasing concentration of humic acid causes a shift of the optimum to lower pH values because more anions are present to neutralize aluminum, and therefore less OH-ions are needed (Fig. 10). In this graph mass ratios are plotted (mg humic acid (HS per mg Al) where the ratio of 1 g humic acid to 1 g aluminum corresponds to 8.1 equivalents humic acid to 0.111 equivalents of aluminum.

The use of a flocculant aid such as polyacrylamide (PAM) or polyacrylic acid (PAS) does not change markedly the range of flocculation. It gave an

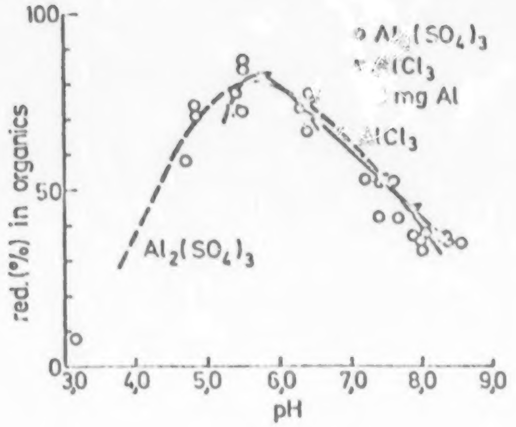


Fig. 6 Comparison of elimination of humic acid by $AlCl_3$ and $Al_2(SO_4)_3$
10 ppm HS
0.111 mmol Al/l, tap water

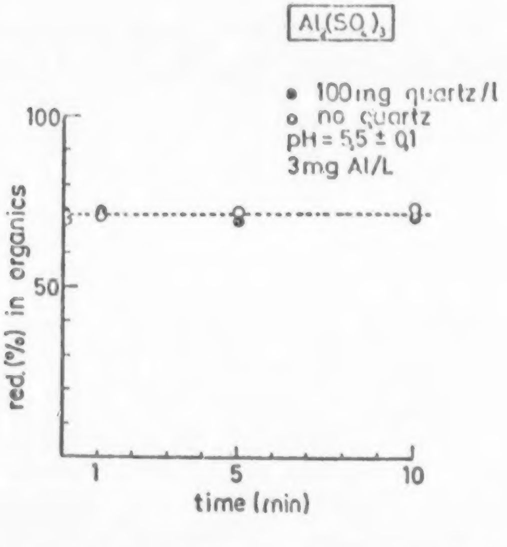


Fig. 7 Influence of the way of dosing the flocculant on elimination (same conditions as in Fig. 6)

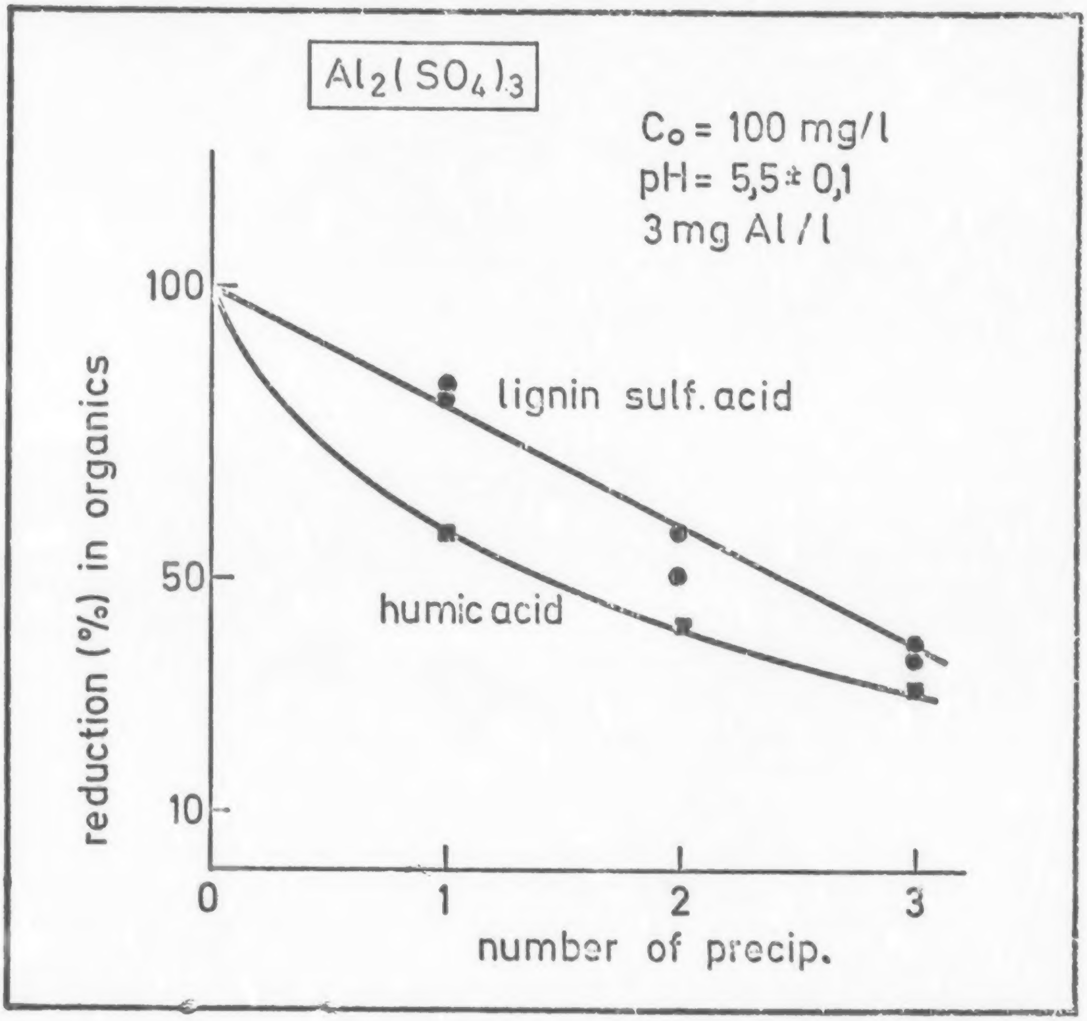


Fig. 8 Elimination of organic material by dosing the flocculant in single steps
100 ppm organic matter

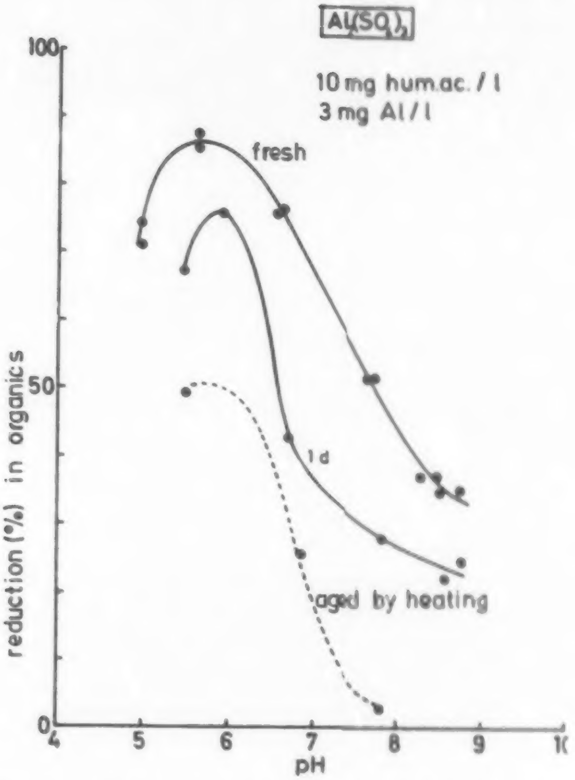


Fig. 9 Influence of the age of floc on elimination of humic acid
10 ppm HS, tap water

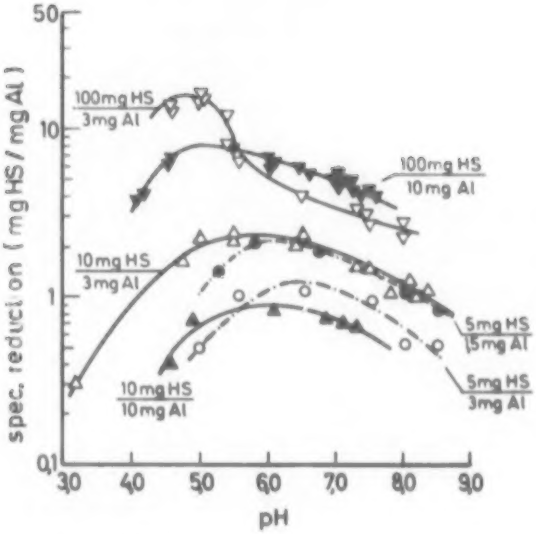


Fig. 10 Elimination of humic acid (HS) by varying the addition of aluminum.

improvement in settling velocity of flocs but not in turbidity removal.

Best results could be obtained by the nonionic flocculant polyacrylamide (PAA) with a molecular weight of 5.10^6 when it was added together with the primary flocculant (Fig. 11).

It was found that the pH range of successful flocculation could be altered depending on whether pH adjustment was made prior to or after the addition of flocculant. As shown in Fig. 12 it is possible to broaden the pH range of successful removal by lowering the pH before the addition of the flocculant to the value pH_d and then, after the addition, to adjust the pH on the desired value.

Pretreatment by ozone did not improve flocculation. The ozonation produced even more soluble substances, as a result the removal of organic material deteriorated (Fig. 13).

Under similar conditions addition of multivalent cations to natural systems causes a very pronounced flocculation effect. This is dependent on both the functional groups and the molecular weight of dissolved organic material. One component of humic acid, the hymatomelanic acid, shows such a behaviour as was observed also with congo red and lignin sulfonic acid.

The hymatomelanic acid was extracted from the commercially available product "humic acid" from ROTH, Germany, which is an extract made from peat. This product was dissolved in sodium hydroxide. After filtration which removed undissolved matter hydrochloric acid was added. The precipitate consists of humic acids and hymatomelanic acid. After extraction with ethanol the hymatomelanic acid which dissolves in ethanol was obtained by evaporation. The end product had an acid number of 5.1 equivalents per gram. In order to obtain similar conditions as with humic acid the 1.5-fold amount in grams was added for the experiments shown in Fig. 14. Even the presence of calcium ions caused flocculation (Fig. 14). Similar curves were obtained with polyacrylic acid (14). In order to eliminate the influence of bivalent ions, deionized water was used for the experiments, the results of which are shown in Fig. 14. One can observe corresponding curves for the reduction in

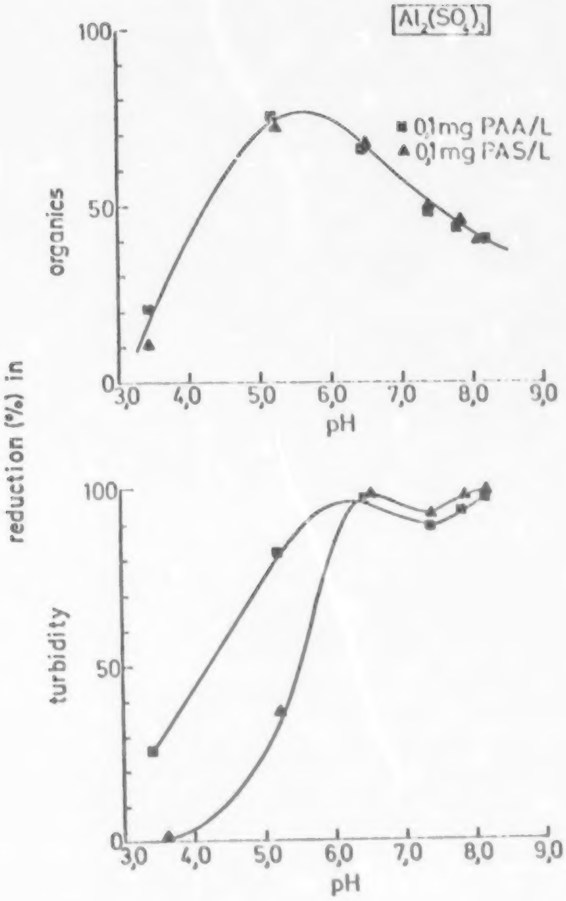


Fig. 11 Influence of flocculant aid on elimination of humic acid (HS)
10 ppm HS, tap water, 100 ppm SiO_2 0.111 mmol Al/ℓ
0,1 ppm polyacrylamide (PAA) resp. polyacrylic acid (PAS)
simultaneous dosage of flocculant and flocculant aid.

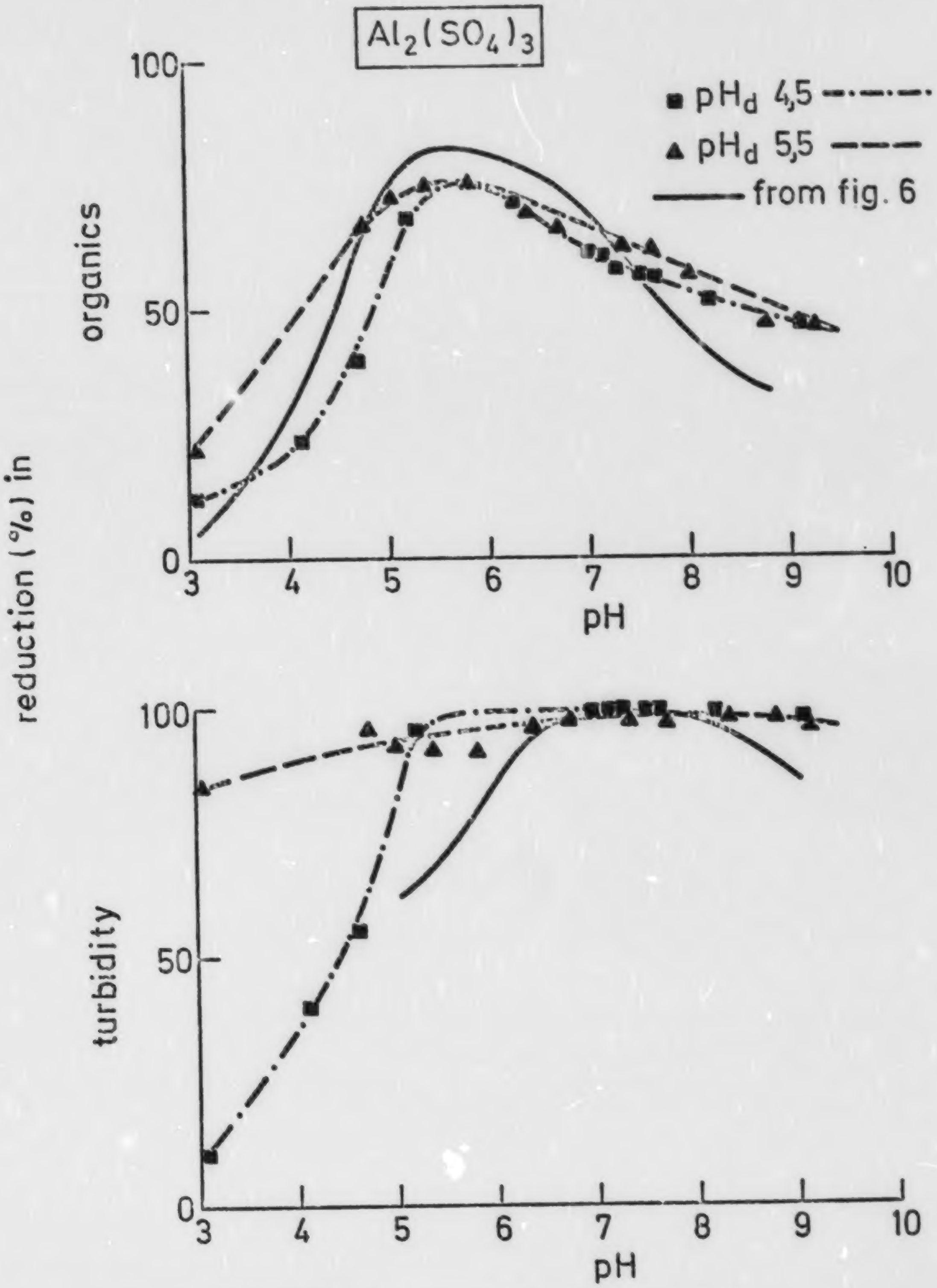


Fig. 12 Influence of pH on elimination of humic acid (HS)
10 ppm HS, tap water, 100 ppm SiO_2, 0.111 mmol Al/l

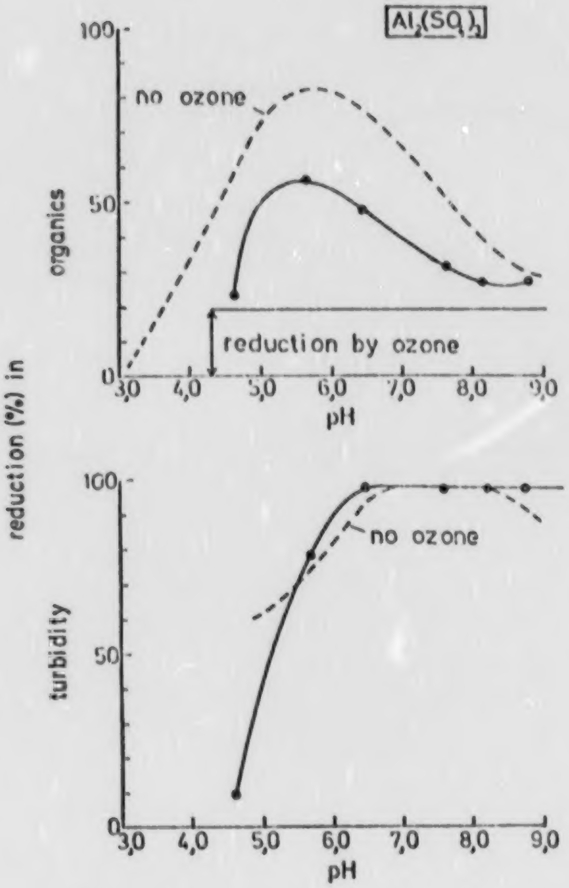


Fig. 13 Influence of ozonization
10 ppm HS, tap water
0.111 mmol Al/l. 2.8 ppm O_3

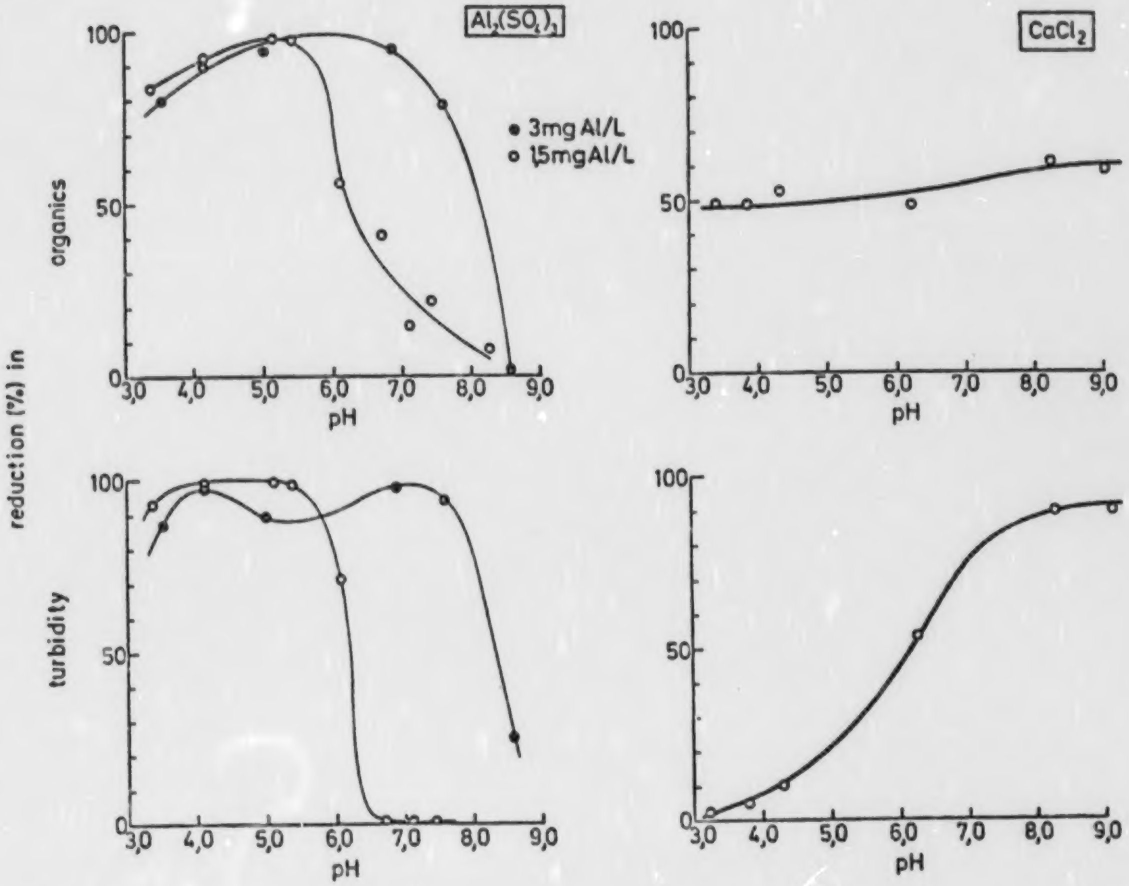


Fig. 14 Elimination of hymatomelanic acid
15 ppm hym. acid, deionized water
100 ppm SiO_2

organics and turbidity when aluminum sulfate is added. The range of reduction is extended if more aluminum is present. The decrease of the curves with higher pH is caused by the hydrolysis of aluminum. When bivalent cations are added removal of organics occurs at higher pH-values as well as it is observed in Fig. 14 where calcium cloride was added. However, there the enmeshment of quartz particles in the precipitate occurs only at higher pH-values. This may be due to the fact that the dissociation of the acid increases and the intermolecular bonding between the polymer molecules predominates. As a result, voluminous networks are produced where the particles are enmeshed and tied up by multivalent cation bridges to the polymer.

Results which were more similar to those with fulvic acid were obtained with samples of two rivers such as the river Rhine near Karlsruhe (Maxau) and the river Ruhr near Milheim. They were selected because they show a very different behaviour concerning the purification for drinking water. As is seen in Fig. 15 for both water samples the optima of reduction in organics and turbidity differ if $Al_2(SO_4)_3$ or $FeCl_3$ was added. This means that at the pH value at which maximum turbidity removal is obtained not all removable organic substances are precipitated. Only by adding PAC both turbidity and organic material removal can be matched. The differences between $Al_2(SO_4)_3$ and $FeCl_3$ are similar to those which are found for the other systems: maximum removal of organic matter occurs at a low pH when $FeCl_3$ is added; the precipitates formed by adding $FeCl_3$ are better able to enmesh colloidal material, as is seen by the two optima in Fig. 15. This was observed in a more pronounced manner for humic acid removal. For both rivers removal of organics is greater with $FeCl_3$.

For this system too ozoniation does not increase the reduction since ozonization causes an increase in solubility of organic matter, and therefore a deterioration of precipitation (Fig. 16).

Conclusions

Surface waters contain both dissolved organic and colloidal material. It is possible to choose the treatment conditions in such a way that maximum removal

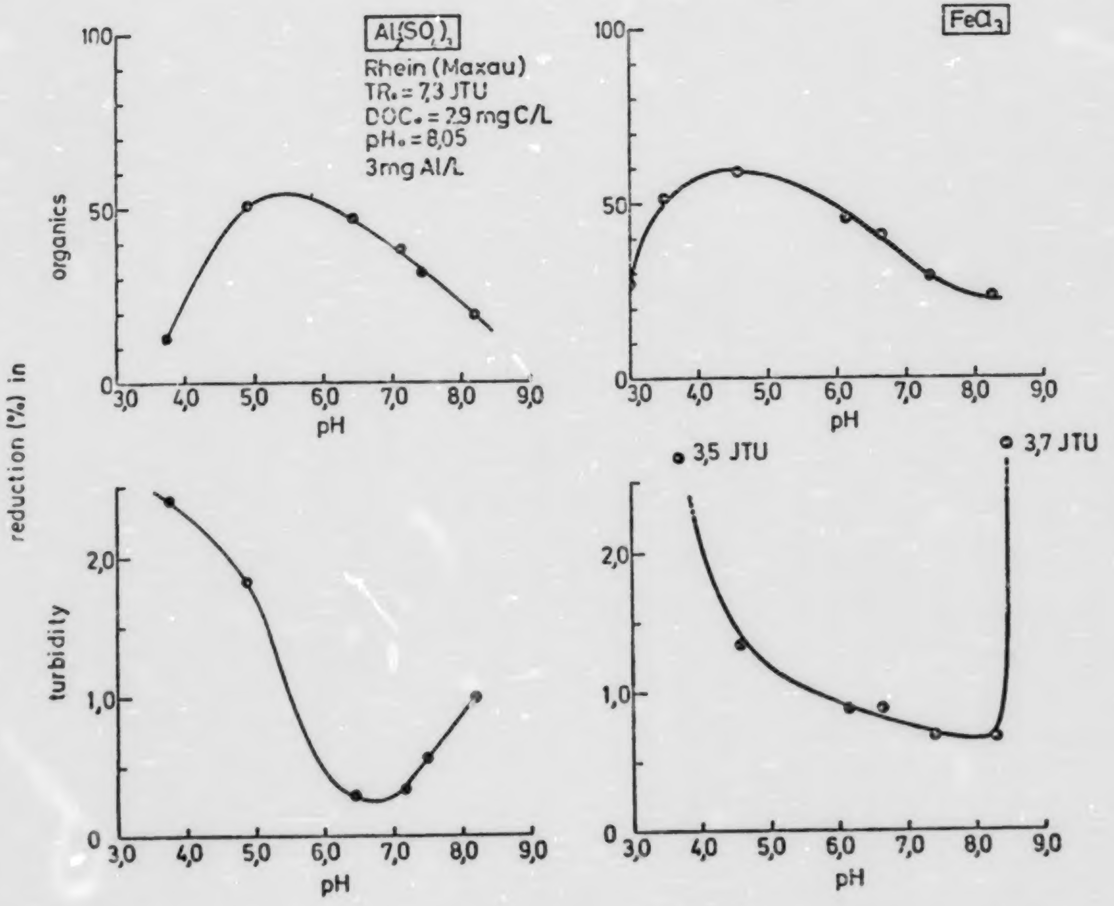


Fig. 15 Reduction of organic content in
a) river Rhine
0.111 mmol Al and Fe/1

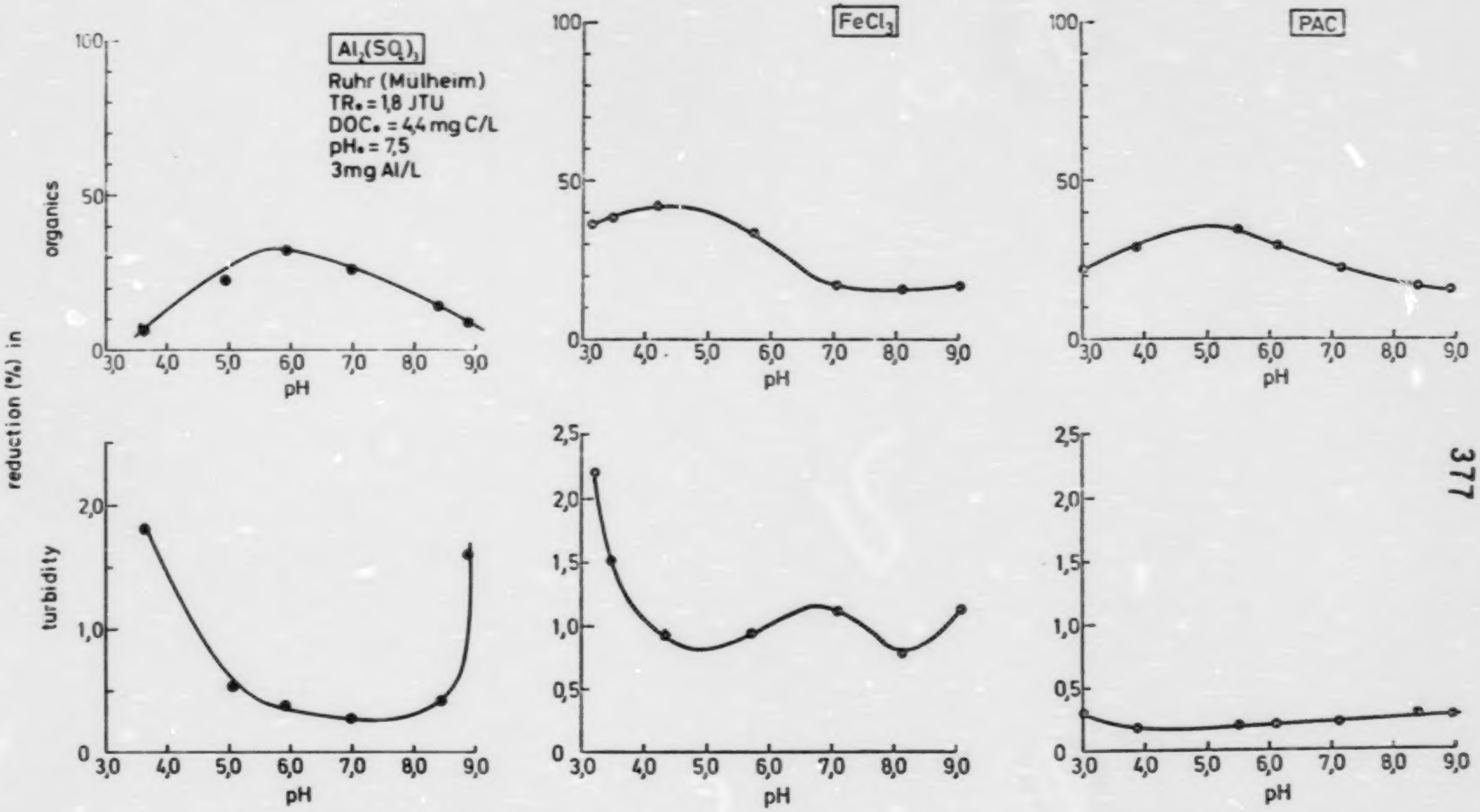


Fig. 15 Reduction of organic content in
b) river Ruhr
0.111 mmol Al and Fe/l

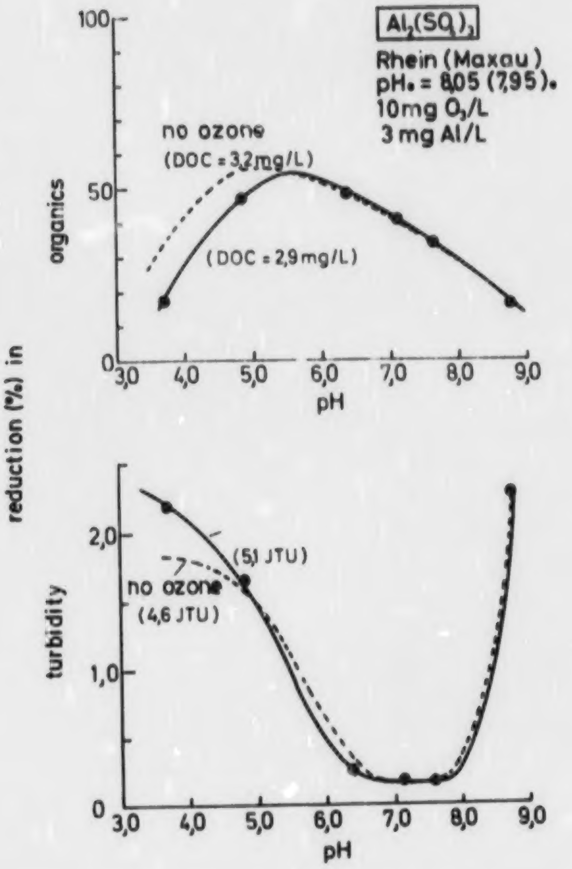


Fig. 16 Influence of ozone on elimination of organic compounds

of turbidity and dissolved organic material takes place at the same time. For this procedure the type of flocculant and the pH are the main variables. Because physical operation parameters such as stirring velocity and time do not influence the precipitation of the dissolved organic compounds, optimal chemical parameters can be found in the classical jar test.

STUDY ON THE ADSORPTION PROPERTIES OF ALUMINIUM OXIDE AND ITS APPLICATION FOR THE PURIFICATION OF GROUND WATER CONTAINING HUMIC SUBSTANCES

by S.H. Eberle, H. Stöber and D. Donnert, Karlsruhe

Activated carbon, already long in use for the purification of water, adsorbs hydrophobic, slightly polar organic substances and only to a smaller extent the hydrophilic and strongly polar organic acids. But the latter ones, according to recent investigations, make up the main fraction of organic carbon in water (EBERLE 1973,1974; KOPPE 1972; KEMPF 1975). This conforms with the practical experience that water treatment with activated carbon results in a partial elimination of the organic carbon. Therefore, the application of an adsorbent retaining preferably organic acids could be of help to solve a number of existing problems in the purification of waters. Applying it together with activated carbon should make possible a complete purification of waters, mainly polluted with non-biodegradable organics.

In the search for an adsorbent of this kind suitable for technical application we investigated which organic compounds, dissolved in water,are removed with aluminium oxide. Its ability to adsorb organic substances has been known for a long time. In 1906 it was used for the separation of different organic compounds from each other and not for their separation from water. Evidently, no attention was paid for its use for this purpose. Finally, in 1974 PLOETZ reported on successful experiments concerning the purification of the waste waters from a wood pulp bleaching plant with aluminium oxide. A large-scale plant employing this method is due to come into operation in a pulp and paper factory in Baienfurt in 1976. Other aluminium compounds have been in use for a long time for water purification. Aluminium hydroxide, prepared in situ, is a standard flocculating agent in water treatment. It has a broad application spectrum due to its interactive and sequential action of several effects, such as removal of turbidity, destabilization of colloids, chemical precipitation and co-precipitation and adsorption on the floc (EBI, 1967). In 1914 FREUNDLICH found that, in doing so, organic acids were also removed from water (KRCZIL, 1938). Solid aluminium oxide, pretreated at higher temperatures, on the other hand, is thought to be effective, principally due to its adsorption properties. Therefore, one cannot expect at once the same broad spectrum of action. During flocculation with aluminium salts the "adsorbent" is used only once. It results in the elimination of the organic compounds from the water treated, but not in their destruction. Indeed, the subsequent treatment of the resulting sludge is a serious problem. On the other hand, the idea of using solid aluminium oxide for the purpose is motivated by the fact that it can be regenerated thermally, while at the same time achieving the combustion of the organic compounds.

Studied aluminium oxides

The aluminium oxides, chromatographic and technical ones, used for this research, are summarized in Table 1.

Table 1: Data on the tested aluminium oxides

	BET surface area m^2/g	bulk weight g/cm^3	grain size mm
M90S "for column-chromatography"	95	1.0	0.1
CTG-80 H activ. alumina	130	1.0	0.07 - 0.15
FL 300 H activ. alumina	300	0.85	0.05 - 0.15
COMPALOX, compressed activ.alumina	200	0.87	1 - 3

The X-ray diagram shows the lines of γ-Al_2O_3 except in the case of the FL 300, which has an X-ray amorphous structure. From the chemical point of view they are not pure, but oxides hydrated at least on the surface. The water content is between 2 and 10 per cent, depending on the applied activation temperature (300 - 700 °C).

The properties important from the point of view of its practical application and adsorption capacity are: the BET surface area, the size of pores, the grain size and the mechanical stability. Concerning the BET areas, all the tested oxides were inferior to activated carbon. On the other hand, the pore size is about 100 Å, much greater than that of activated carbon. For the latter, the pore diameters required for adsorption lie between 5 and 20 Å, as given in the literature.

In the course of our own investigations, it appeared that the basicity of the oxides is another important property. The oxides contain in their original state, due to the manufacturing process, up to 1 per cent of sodium, and therefore give in an aqueous suspension a strongly alkaline reaction. But in almost all instances a high pH value is unfavourable for the elimination of organic substances. The sodium may be washed out with diluted mineral acid, so that afterwards the aqueous suspension of the oxide has a pH value between 4.5 and 7. The pH value of a 10 %-aqueous suspension is used as a reference number for the acidity of the oxide.

The granular COMPALOX is intended for application in fix-bed columns. Using fine oxide (<0.5 mm) the expanded bed technique has to be used, whereby water flows onto the oxide bed from below at a limited speed, and with an appropriate granular fraction a sharp separation of the suspension bed takes place as the liquid flows up. For the expansion of the bed from grain size 0.07 to 0.1 mm the relation $\Delta V/V = 0.3\ S$, for streaming speeds $S < 6$ m/h was found.
The price of the tested technical oxides lies between 800 and 1500 DM/ton.

Adsorption of pure organic compounds from water

Experimental technique

It was expected that hydrophobic compounds such as benzene, nitrobenzene etc. would not have a high affinity for aluminium oxide, and therefore no experimental work was undertaken with these substances. On the other hand, a great deal of aromatic acids, bases and phenols were tested by adding 1 or 2 g of the oxide to 50 ml of an aqueous solution of the compound or the waste water and shaking slowly for 24 to 48 hours. The determination of the residual concentration was carried out after membrane filtration, for pure compounds spectroscopically, while for the not so well-defined compounds, or for waste waters, by measuring the dissolved organic carbon (DOC). The difference between initial and residual concentrations expressed in per cent of the initial concentration is referred to as the elimination. The term "adsorption" should be used for these data only with caution since other mechanisms such as precipitation may be responsible for the removal of part of the organic material.

During experiments with some compounds, e.g. ligninsulphonic acid, precipitation was visually observed in the bulk solution.

The following formulas were used for the calculation of the data for isotherms:

residual concentration from UV measurements: $C = \frac{E}{E_o} \cdot C_o$ (mg/l)

oxide load: $Q = (C_o - C) \frac{V}{m}$ (mg/kg)

where C_o = initial concentration (mg/l)
E_o = initial extinction at the measuring wave length
E = extinction after equilibrium restoration at measuring wave length
V = dissolving volume for the charge in litre
m = oxide amount for the charge in kg

Adsorbing capacity and functional groups

The dependence of the adsorption capacity on the type of functional group is shown in Table 2 for some representative compounds.

Table 2: Elimination of aromatic compounds with aluminium oxide. Charge: 50 ml solution containing 500 mg/l of the compound (1 g Al_2O_3)

compound	oxide/pH/ method of measurement	elimination
p-toluidine	CTG80/pH5/UV	6 %
p-cresol	CTG80/pH5/UV	9 %
p-chlorophenol	CTG80/pH5/UV	23 %
p-nitrophenol	CTG80/pH5/UV	14 %
picric acid	M90S/3	53 %
p-toluene sulphonic acid	CTG80/pH5/UV	41 %
3-aminobenzene sulphonic ac.	CTG80/pH5/UV	67 %
naphtalene-1-sulphonic acid	CTG80/pH5/UV	26 %
4-aminonaphtalene-1-sulphonic acid	CTG80/pH5/UV	43 %
pyren-sulphonic acid	M90S/pH3/DOC	99 %
naphtalene-1-sulphonic acid	M90S/pH3/DOC	51 %
naphtalene-2,6-disulphonic acid	M90S/pH3/DOC	85 %
naphtalene-1,3,6-trisulph. acid	M90S/pH3/DOC	95 %
naphtalene-1,3,5,7-tetra-sulphonic acid	M90S/pH3/DOC	90 %
benzoic acid	M90S/pH5/UV	64 %
p-hydroxybenzoic acid	CTG80/pH5/UV	80 %
phtalic acid	M90S/pH5/UV	86 %
pyridine-3-carbonic acid	M90S/pH5/UV	63 %
pyridine-2-carbonic acid	M90S/pH5/UV	60 %—
thiophene-2-carbonic acid	M90S/pH5/UV	53 %
8-hydroxyquinoline-5-sulph.a.	M90/pH3/UV	78 %
Congo red	M90/pH3/UV	99 %
ligninsulphonic acid	COMPALOX/pH3/DOC	80 %
humic acid	M90SS/pH5/DOC	56 %
waste water from a cellulose bleaching plant DOC = 290	COMPALOX/pH3/DOC	76 %

The results may be summarized as follows:

- all aromatic compounds containing dissociable hydrogen atoms are adsorbed by Al_2O_3. This is valid as well for carbocylic and for heterocyclic compounds;
- the adsorption capacity is increasing in the sequence bases<phenols<acids if analogous compounds are compared;
- with increasing number of acidic groups in a molecule the adsorption rate goes through a maximum, which in the sequence of the naphthalene sulphonic acids lies at the naphthalene-1,3,6-trisolphonic acid;
- compounds containing basic and acid groups (e.g. substantive dyestuffs) are extraordinarily well adsorbed;
- carbonic acids normally are adsorbed better than the corresponding sulphonic acids.

Generally, the functional acidic hydrogen-containing groups determine whether and to which extent these groups are responsible for the binding onto the oxide. Of course, the nature of the aromatic nucleus and of non-acidic substituents are not without influence, but all experimental results obtained to date point to the conclusion that the existence of H^+-active groups is a condition for a good adsorption onto aluminium oxide.

Influence of the molecular weight

To what extent Al_2O_3 can adsorb organic acids with higher molecular weights is of great interest since this is a weak point of activated carbon. According to Table 3, where the adsorption of several compounds with the same acid groups is shown, the affinity to Al_2O_3 for sulphonic acids is increasing along with the increase in molecular weight.

Table 3: Elimination from water as a function of the molecular weight (1 g M90S, 50 ml, initial concentration 500 mg/l, pH 5)

	Mol. Wt.	elimination
benzene sulphonic acid	158	26 %
naphthalene -1-sulphonic acid	208	74 %
anthraquinone-2-sulphonic acid	288	96 %
ligninsulphonic acid	50 000	48 %
humic acid from Lake "Hohloh"	20 000	69 %
humic acid from turf	40 000	56 %

This tendency is not continued up to the ligninsulphonic acid but, in any case, this compound is also adsorbed fairly well. The same tendency was detected in the case of carbonic acids. Concerning humic acids, it was shown that the sample with lower molecular weight is better adsorbed than that with a higher molecular weight. In the case of the compounds studied in this connection, the extent of elimination is passing a maximum with increasing molecular weight. The initial increase may be understood as the consequence of the increase in mass of the bonding groups which increase with the molecular weight. The decrease for very big molecules may be interpreted as a consequence of the diminishing of the inner surface area. For the application of water purification it is of importance that Al_2O_3 eliminates humic acid and ligninsulphonic acid as well.

Influence of the pH value on the aqueous phase

The pH value was shown to be a significant adjustable parameter, capable of influencing the adsorption.

Fig. 1: Elimination as a function of the final pH (charge: 50 ml - 50 mg substance/l + 1 g M90S)

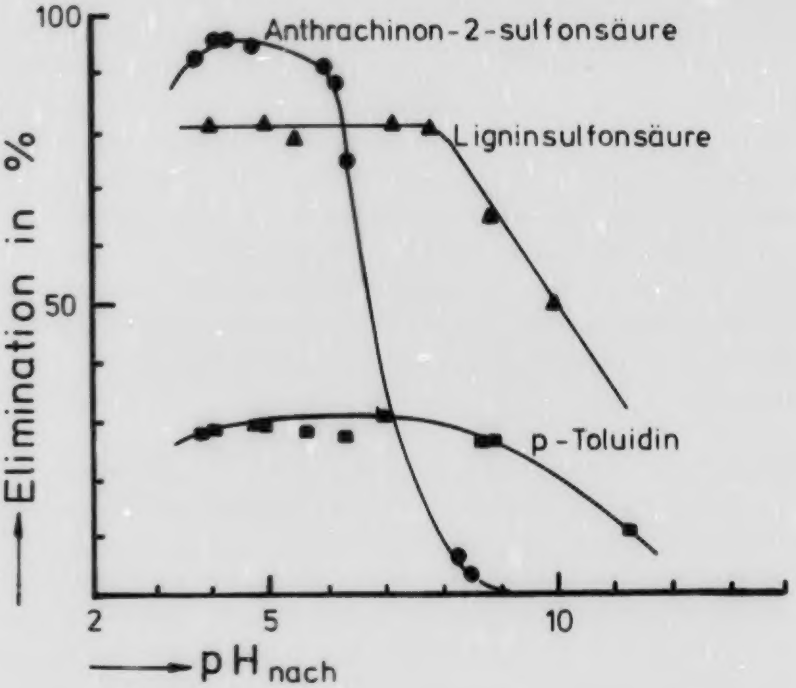


Fig. 1

Anthrachinon-2-Sulfonsäure: anthraquinone-2-sulphonic acid
Ligninsulfonsäure: ligninsulphonic acid
p-Toluidin: p-toluidine
pH_{nach}: final pH

As shown in Fig. 1 with several examples,the elimination is passing a more or less broad maximum with increasing pH, its location of course depending on the type of the compound used, and especially on its acidity. In most cases, already from the pH of 9 onwards, the main part of the organic compounds remains in the aqueous phase. The best range of activity for the elimination of organic acids lies between pH 4 and 6. Therefore, basic oxides giving an alkaline reaction of the aqueous phase show a worse elimination than acidic oxides. If, for example, loaded oxide is treated with a basic buffer solution or sodium hydroxide, desorption occurs. Indeed, the desorption is slow and incomplete, and therefore a chemical regeneration is not very promising.

While adjusting the optimal pH value, the fact has to be considered that by contact with the oxide the pH may change about two units, whereby it increases in strongly acid solution and decreases in strongly alkaline solution. The effect should be measured - particularly if waste waters are concerned - by means of a preliminary test. As aluminium oxide dissolves slowly at a pH lower than 2 or higher than 12, it should not be used under these pH conditions. Apart from the pH value, the presence of inorganic salts has an influence on the elimination attained. In fact, it decreased with increasing salt concentrations in the aqueous phase in the few cases investigated by us. The same behaviour is known for ion exchange resins.

Influence of the size of the inner surface area of the oxide

In Fig. 2 the relative adsorption strength of the oxides is demonstrated as a function of the inner surface area on three organic acids as an example.

The low-molecular compounds vanillic acid and anthraquinone-2-sulphonic acid are better eliminated the greater their inner surface area. A behaviour of this kind is to be expected if the oxides are differing only in the size of the inner surface area and not in their topochemical qualities. For dyestuff waste-waters containing mainly compounds with a molecular weight between 300 and 600 too, we found that the oxide with the highest BET surface area has always the highest elimination capacity.

For ligninsulphonic acid, a completely different tendency is observed: its elimination is less satisfactory with increasing inner surface area of the oxide. We are interpreting it as an effect of the pore size. For the macromolecular ligninsulphonic acid with a diameter of 30-90 Å (KRCZIL, 1938), only part of it can reach the inner surface, depending on the pore size.

Fig. 2: Elimination of organic acids as a function of the inner surface area of Al_2O_3 (charge 50 ml - 1 g substance/l + 1 g oxide)

This is in accordance with the fact that ligninsulphonic acid is best adsorbed by the oxide type M150(T),having the greatest pore diameter of 150 Å. For other oxides the pore diameter is decreasing with increasing surface area, and therefore the capacity for the adsorption of ligninsulphonic acid is also decreasing.

Isotherms

Some representative examples of isotherms are shown in Fig.3 where in a double-logarithmic diagram the oxide load is plotted against the residual concentration. Within a range of two powers of ten of the concentration, or the oxide load resp., the measured points are in a straight line. Therefore, the adsorption may be described by the equation of FREUNDLICH.

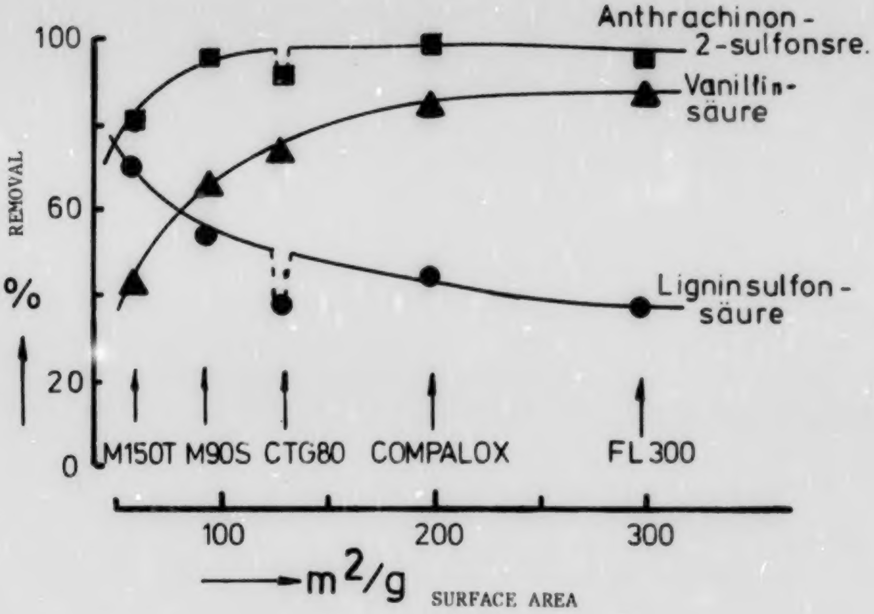


Fig. 2

Anthrachinon-2-Sulfonsäure: anthraquinone-2-sulphonic acid
Ligninsulfonsäure: ligninsulphonic acid

Vanillinsäure: vanillic acid

Fig. 3: Adsorption isotherms of organic compounds ($pH_{init.} = 5$)

$q = k_F \cdot c^n$

q in mg/kg

c in mg/l

This is also valid for most of the other tested compounds. But in some cases it was found by means of more intensive measurements that the isotherm is obeying the Langmuir-equation. This is, for instance, the case for vanillic acid, as ROHMANN detected during his research work on the kinetics of adsorption on Al_2O_3 (ROHMANN, 1975).

Oxide loading and costs of water treatment

For the discussion of the attainable oxide load in dependence of the initial concentration the FREUNDLICH equation in logarithmic form may be applied:

$$\lg q = \lg k_F + n \cdot \lg c \qquad (1)$$

Rearangement of the equation results in:

$$\lg k_F = \lg q - n \cdot \lg c \qquad (2)$$

If lg q (the oxide load at equilibrium) and lg c (the residual concentration at equilibrium) are kept constant, the logarithm of the adsorption constant is a linear function of the adsorption exponent. Here lg c is the slope of the straight line. Technical realization of the purification by adsorption will be done preferably by countercurrent flow and removing that portion of the oxide on the starting point of the column which has reached an equilibrium state with the substance. Therefore, for the final state of the load, the residual concentration is equal to the inflow concentration. Thus, equation 2 is describing

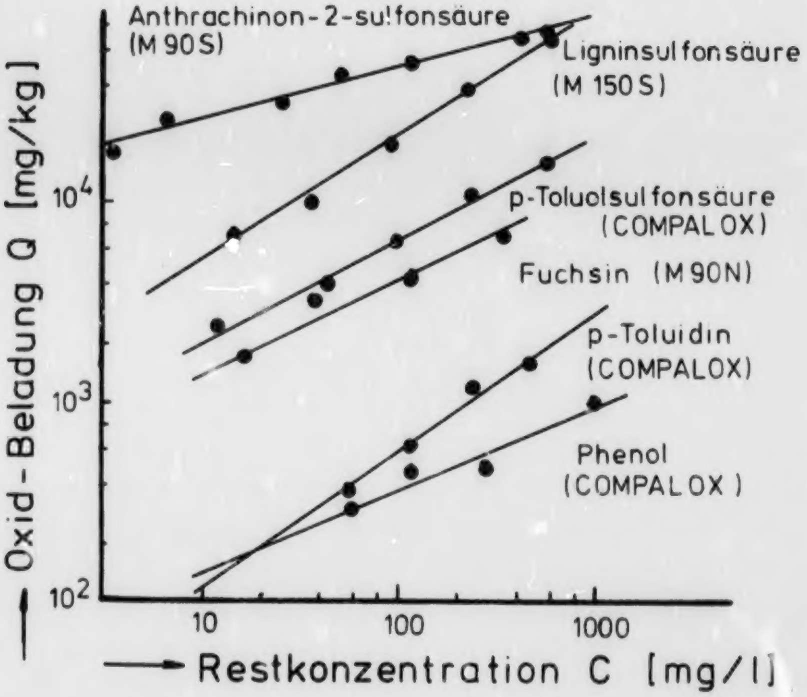


Fig. 3

Anthrachinon-2-Sulfonsäure: anthraquinone-2-sulphonic acid
Ligninsulfonsäure: ligninsulphonic acid
p-Toluidin: p-toluidine

Oxid-Beladung: oxide loading
p-Toluolsulfonsäure: p-toluene sulphonic acid
Restkonzentration: residual concentration

the straight line of those combinations of lg k and n-values which, at a certain inlet concentration, result in a certain loading. In a diagram "lg k vs. n" each compound occupies one point. Each combination of lg c and lg q forms a boundary line, above which lie such compounds which by the used inflow concentration reach a higher loading than given by "lg q".

In Fig. 4 the FREUNDLICH constants, obtained for various compounds and oxides, are plotted in such a diagram. 10^4 mg/kg, equalling 1 per cent, was chosen as a fixed value of loading, which normally is the economical limit. All acids examined yielded loads greater than 1 per cent for an inflow concentration of 1000 mg/l. Far worse is the case with simple phenols and aromatic amines, as water purification by means of Al_2O_3 is not possible. For many acids a load of 1 per cent is still obtained for concentrations of 100 mg/l or a higher load at correspondingly higher concentrations. Only few compounds are attaining $q = 1$ per cent for the inflow concentration of 10 mg/l. To this group the higher naphtalene-sulphonic acids belong, which are causing many problems for waste waters of pigment and pharmaceutical manufacturing plants. Humic acid, which is creating problems during the processing of drinking water, also belongs to this group.

Fig. 4: FREUNDLICH constants of the elimination of organic compounds with aluminium oxide from water

A load of 1 per cent for an inflow concentration of 100 mg/l means an oxide demand of 10 kg/m^3. To estimate the costs of water treatment, it can be assumed that the price for the regeneration of 1 kg loaded oxide is about 0.15 to 0.20 DM, including investment costs for the whole plant and running charges for the adsorption and regeneration process (rotary kiln). The oxide demand given above corresponds to operating costs of 1.5 to 2 DM/m^3. Only in rare cases it may exceed

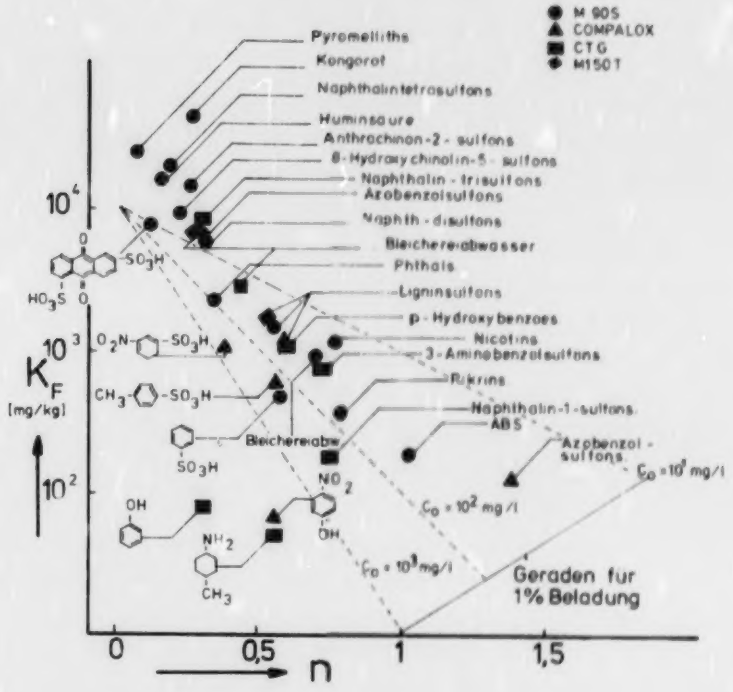


Fig. 4

Bleichereiabwasser: waste water from a bleaching plant

Geraden für 1 % Beladung: lines for 1 per cent loading this order of magnitude for water purification. This means that Al_2O_3 can be used with advantage for waste waters of high concentration prior to biological treatment. However, for some compounds the isotherm shows suitable oxide load values for lower inflow concentrations too. For humic acid, for instance, the oxide demand lies at 0.5 kg/m^3 for an inflow concentration of 10 mg/l,and therefore the purification costs are about 0.07 DM/m^3. From the results on the studies of pure compounds it may be concluded that the application of aluminium oxide is promising for all kinds of aromatic compounds containing acid groups, especially for acids with high molecular weights.

Experiments with waste waters

The adsorption isotherms of several selected waste waters were measured, and for comparison percolation experiments in multicolumn set-ups were carried out (3 to 5 columns, each containing 200 - 400 g oxide, contact time 10 - 20 minutes per stage).

As shown in Table 4, the oxide consumption, taken from the isotherm, lies between 6 and 30 kg/kg C for the relatively concentrated waste waters from production. However, in the percolation experiments it was much lower. Evidently, well-adsorbable substances accumulate from mixtures onto the oxide, whilst in some cases compounds with poor adsorption properties are penetrating sooner. In this case it is a question of optimization of the process which degree of elimination and which oxide consumption value is to be chosen. For the effluent of an activated sludge process studied, the oxide demand for a total elimination of the DOC is extremely high and therefore an application of Al_2O_3 in this case hardly seems acceptable from an economical point of view.

Table 4: Specific oxide consumption value for waste water purification with Al_2O_3

	Specific oxide consumption	
	isotherm	percolation experiment
1) Porteous filtrate DOC-4500 mg/l, pH 3 FL300S	15 kg/kg C	15 kg/kg C
2) waste water of a sulphite pulp plant DOC 280 mg/l, pH 4	30 kg/kg C	13 kg/kg C
3) waste water of an anthraquinone pigment production FAM DOC 900 mg/l, pH 3 M90S	29 kg/kg C	14 kg/kg C
4) Dye liquor from a substantive dyestuff DOC 380 mg/l, pH 7 FL300S	6 kg/kg C	6 kg/kg C
5) Outflow of an industrial activated sludge step DOC 87 mg/l, pH 5 COMPALOX	360 kg/kg C	---

Tests with ground-water containing humic substances

Isotherms

To confirm the applicability of the oxide consumption value, obtained with a standardized humic acid, to other types of oxides and natural substances present in water, the isotherms of two "organic acids" separated from water by means of the ALAMIN process (EBERLE, 1973) were measured. The first substance in question was an extract from water taken from the river Rhine at Wiesbaden, containing ligninsulphonic acid as the main pollutant. The second one was an extract from gravel-filtered water from the waterworks at Fuhrberg near Hanover which contained humic acid. The oxide used for the measurement of isotherms and water treatment tests was acid-treated COMPALOX (1 to 3 mm). The concentration parameter measured in all cases was the DOC.

For both extracts the isotherm is higher than that of ligninsulphonic acid, and lower than that of humic acid.

Fig. 5: Adsorption isotherms of high molecular organic acids and ALAMIN extracts from waters ($pH_{init.}$ = 5, oxide acid-treated COMPALOX)

The isotherm plotted for the genuine COMPALOX is also a good illustration of the poor adsorption effect of a basic oxide. The very low elimination can be attributed to the alkaline reaction of the aqueous phase, caused by this oxide. After treatment with acid, the same oxide has an adsorption effect, increased by some orders of magnitude , as shown by the isotherms.

From the isotherm it can be concluded that the oxide demand for the elimination of DOC from a gravel-filtered water, with DOC = 10 mg/l, should amount to approximately 0.7 kg/m^3.

Laboratory tests using columns

The percolating experiments were carried out using three glass columns, 20 x 300 mm, with a retention time of about 30 minutes for each column. Each column was filled with 200 g of acid-treated COMPALOX. The average measured values of the inflowing water were as follows:

pH = 4
DOC = 7 mg/l
$KMnO_4$ =16 mg/l

Extractable by ALAMIN: approx. 60 percent of DOC

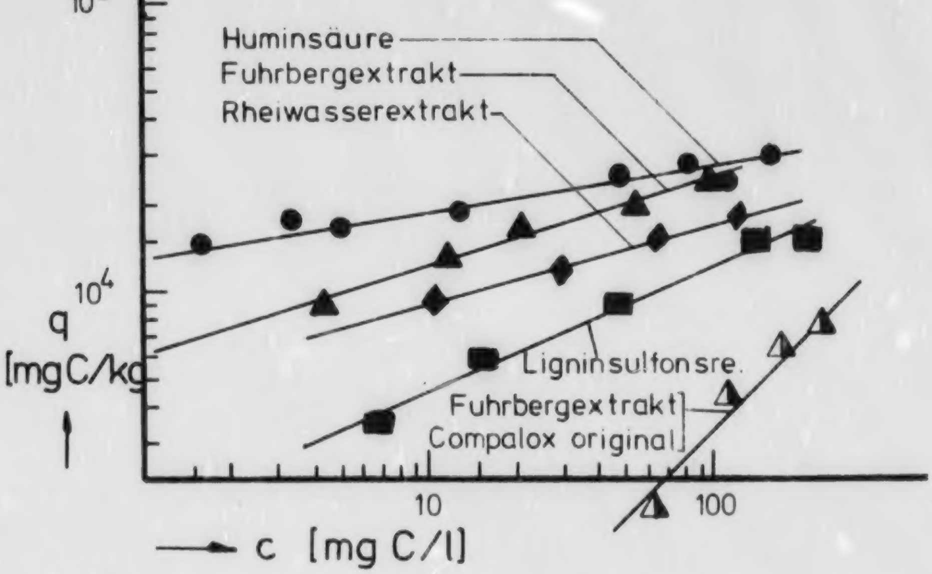


Fig. 5

Huminsäure: humic acid

Fuhrbergextrakt: extract from Fuhrberg plant

Rheinwasserextrakt: extract from water from river Rhine

Ligninsulfon sre: Lignin sulphonic acid

The result of the longest test carried out in this connection (2 months) is presented in Fig. 6.

Fig. 6: Data of a laboratory percolating test with ground-water gravel filtrate from Fuhrberg (3 x 200 g, acid-treated COMPALOX)

After percolating 50 bed volume the elimination efficiency of the first column decreased to 60 %, and after about 500 bed volume a constant level was reached: first column 55 %, second column 60 %, third column 65% elimination. Up to the end of the experiment, after the percolation of 1500 bed volume no further decrease was observed.

Apparently, the water contains two groups of material, of which only one, with a fraction of 60 %, adsorbs well on Al_2O_3. The similarity of this percentage with the DOC fraction extractable by ALAMIN suggests that ALAMIN and Al_2O_3 belong to the same group of substances.

At the end of the test the load of the oxide of the first column was about 0.6 %, that is almost the saturation load calculated from the isotherm. However, since the column still showed 50 % elimination efficiency, it may be assumed that the capacity of the oxide is considerably higher than the value calculated from the isotherm. Contrary to this "better" experimental result , there is the negative observation that, on the whole, only 60 % to 70 % of DOC can be removed from the water by Al_2O_3. It should therefore be checked whether the thus purified water meets the requirements. Presumably it is not the aim of a waterworks to reach a zero value of DOC.

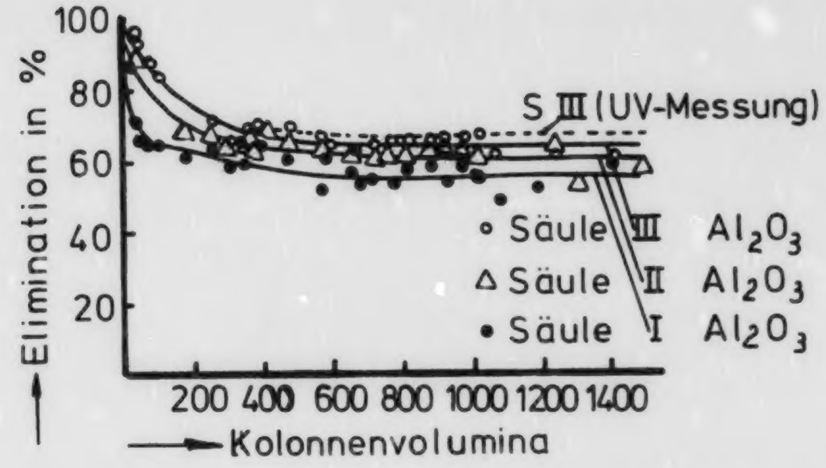


Fig. 6:

UV-Messung: UV measurement

Säule: column

Kolonnenvolumina: Bed volume

Pilot tests at Fuhrberg

To confirm the laboratory test results, the experiment was repeated, on a somewhat larger scale, at Fuhrberg (near Hanover), but it is still by some orders of magnitude smaller than the throughput of a waterworks.

Fig. 7: Pilot plant for adsorptive treatment of water with Al_2O_3 (3 columns, 52 x 1000 mm)

The transportable apparatus (see Fig. 7) consists of a sand-filled prefilter, two series-connected columns, 52 x 1000 mm, each filled with 1.8 kg of genuine COMPALOX, and a third column of the same dimensions, filled with 0.7 kg of activated carbon, type LS SUPRA. This charge was selected expecting that the carbon would adsorb the substances not adsorbed onto Al_2O_3. The gravel-filtered water is pumped through the apparatus with a rate of 4 m/h = 8 l/h. The calculated retention time within the whole apparatus is 0.7 h.

Fig. 8: Data of a percolation test with the Al_2O_3-activated-carbon pilot plant at the Fuhrberg waterworks (2 x 1.8 kg COMPALOX-Original, 1 x 0.7 kg LS Supra)

Fig. 8 shows the results after four weeks of operation with the first charge of adsorbents. The efficiency of Al_2O_3 is lower than that in the laboratory test. However, it must be considered that COMPALOX-Original was used there and not the much better acid-treated COMPALOX. Furthermore, the feed water had an acidity of pH 8 and not of pH 4 as in the laboratory test. The most important result is the fact that the combination of Al_2O_3 with adsorbent carbon permits the total purification of the Fuhrberg water. This result could not be obtained by any of the other methods used at Fuhrberg so far. The exact

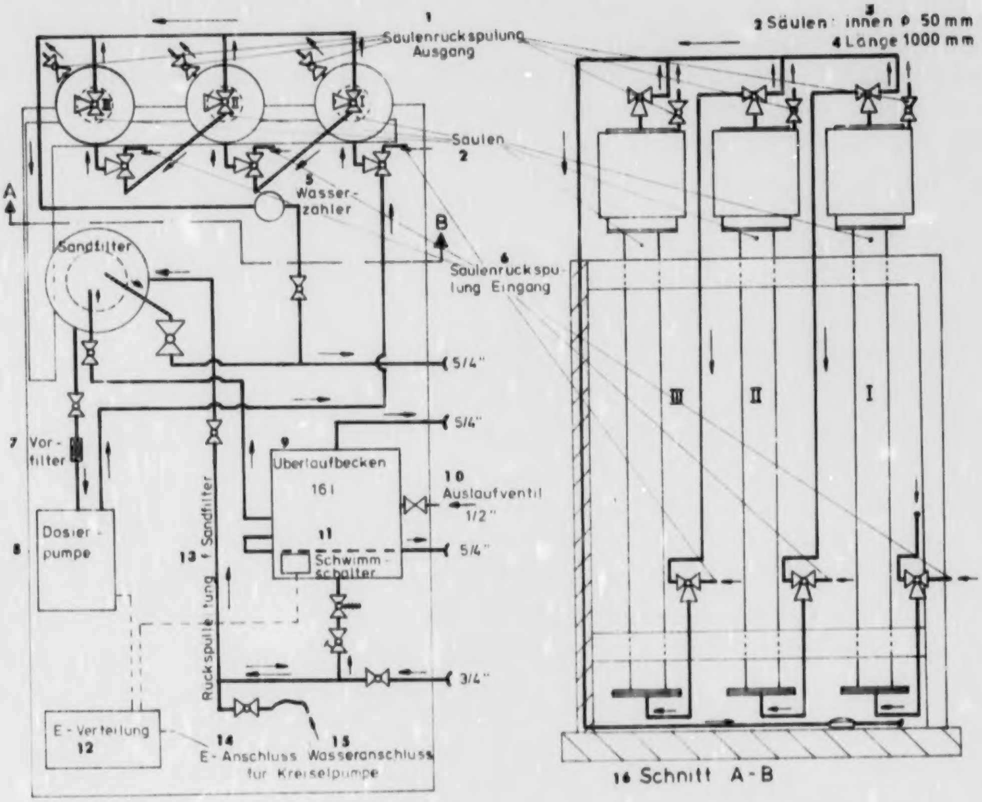

1 Saulenruckspulung Ausgang
2 Säulen: innen ø 50 mm
4 Länge 1000 mm
Saulen 2
5 Wasser-zahler
A
B
Sandfilter
6 Saulenruckspulung Eingang
5/4"
5/4"
7 Vor-filter
9 Uberlaufbecken
16 l
10 Auslaufventil 1/2"
11
Schwimm-schalter
5/4"
8 Dosier-pumpe
13 Ruckspulleitung Sandfilter
3/4"
E-Verteilung 12
14 E-Anschluss
15 Wasseranschluss für Kreiselpumpe
III
II
I
16 Schnitt A-B

Fig. 7: Pilot plant for adsorptive treatment of water with Al_2O_3 (3 columns, 52 x 1000 mm)

1 Saulenruckspulung Ausgang: Columns backwash outlet
2 Saulen: Columns
3 Innen ø: Diameter
4 Lange: Length
5 Wasserzahler: Watermeter
6 Saulenruck spulung Eingang: Columns backwash inlet
7 Vorfilter: Prefilter
8 Dosierpumpe: Dosage pump
9 Uberlaufbecken: Overflow vessel
10 Auslaufventil: Outlet valve
11 Schwimmschalter: Floating level control
12 E-Verteilung: Electronics
13 Ruckspulleitung f. Sandfilter: Backwash pipe for sandfilter
14 E-Anschluss: Electricity inlet
15 Wasseranschluss: Water inlet
16 Schmitt A-B: Cross section A-B

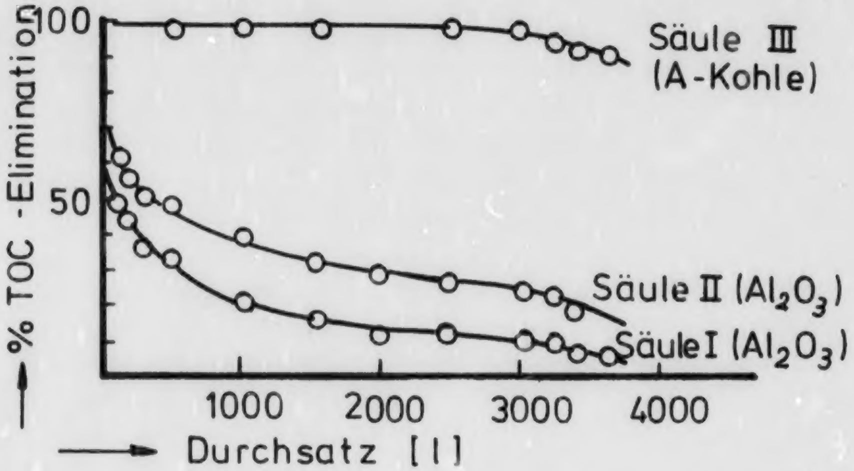


Fig. 8

Säule: column

Durchsatz: throughput

A-Kohle: activated carbon

amount of adsorbents required cannot be specified as yet. First of all, it will have to be established in which way and how often oxide can be regenerated. However, it can be said that the oxide demand should be substantially lower than 0.5 kg/m^3, and the demand of adsorbent carbon lower than 0.1 kg/m^3. The actual demand also depends on the desired degree of water purification. If, for instance, an elimination of 50 % is considered sufficient, then only half the quantity of the respective adsorbent has to be regenerated.

The experiments have shown that there are good prospects for obtaining drinking water,with an adjustable residual DOC content, from ground-waters of the Fuhrberg type, containing humic substances, by using a combination of Al_2O_3 with activated carbon.

USE OF MACROPOROUS ION EXCHANGERS FOR DRINKING WATER PURIFICATION

by
W. Kölle, Hanover

During the early sixties ion exchange resins with macroporous structure became commercially available. The initial reactants for the production of this type of resin are styrene and divinyl benzene, the same as for the production of conventional ion exchange resins. The macroporous structure of the resin is achieved by a special technique of co-polymerisation of the initial reactants. The system of macropores remaines unaffected, also during desiccation. In the soaked state, macroporous resins show therefore two fundamentally different types of porosity: the macropores on the one hand and the gel porosity, caused by the soaking process and corresponding to the porosity of conventional resins, on the other hand. (Heft 8, Engler-Bunte-Institute).

The pore system of macroporous resins is of special importance because it makes the functional groups in the interior of the grains accessible for macromolecular components of natural or polluted water. Among the macromolecular organics, the organic acids play by far the most important role (humic acids, sulphonated lignine). Therefore, macroporous resins are produced as anion exchanger as a rule; there are weak basic as well as strong basic resins available, both allowing a fast and reversible exchange of organic acids, whereas conventional anion exchange resins adsorb organic acids incompletely and release them even more incompletely. As a consequence, the capacity of conventional anion exchangers loaded with water containing organic acids is decreasing continuously, an effect, which is called "fouling".

Macroporous anion exchangers in the OH-form play an important role as fouling resistent exchangers for production of boiler feedwater. It was considered earlier,however, to use macroporous anion exchangers in the Cl-status for additional purification of waters containing humic acids (Martinola 1970, Rüffer 1973). Investigations on the exchange kinetics of macroporous resins, performed at Karlsruhe, showed that the exchange of organic acids is very fast. This is of great importance for the use of these resins in practice (Reicherter 1970, Ladendorf 1971).

Effects of water containing humic acids

The water-works of Hanover performed extensive experimental work with advanced purification of a coloured groundwater with the strong basic anion exchanger Lewatit MP 500 A (Bayer, Leverkusen). It was used at the plant of Fuhrberg, where a water is treated that contains iron, manganese, humic acids, and about 130 ppm of sulphate. With the aid of aeration, chlorination, lime treatment, addition of potassium permanganate, filtration, and break-point chlorination, an iron- and manganese-free drinking water is obtained. However, the dissolved organic carbon of 9 ppm in the raw water decreases only to 6 ppm in the finished water. Former attempts to reduce the content of humic acids by economically acceptable processes (e.g. additional flocculation) were unsuccessful. The first real chance of success originated from the possible use of macroporous exchangers and, recently, by the use of activated alumina (Eberle 1975).

The need for an additional purification of this water results directly from its properties: the simultaneous presence of 6 ppm of organic carbon and of 10 ppm of oxygen results in aerobic bacterial growth. The consequence is a marked tendency to bacterial development in this water. Fig. 1 shows an example for the behavior of the Fuhrberg drinking water. The bacteria-containing sample was taken on the occasion of a routine control of the water distribution system of Hanover and stored in the laboratory at about 10 degrees centigrade during several days. The bacterial count of this sample was ascertained daily by the use of normal gelatin culture dishes. Obviously, after an adaptation period of a few days the bacterial counts increase logarithmically until they come up to about 10^6 per ml. This level remains approximately constant.

Fig. 1

A second disagreeable property of waters containing high concentrations of organics is their high chlorine consumption. The water distribution within the pipe system is therefore a permanent "running match" between the chlorine consumption and the bacterial development.

It has to be emphasized that chlorination of organically polluted water is connected with undesired chlorination reactions which produce chloro-

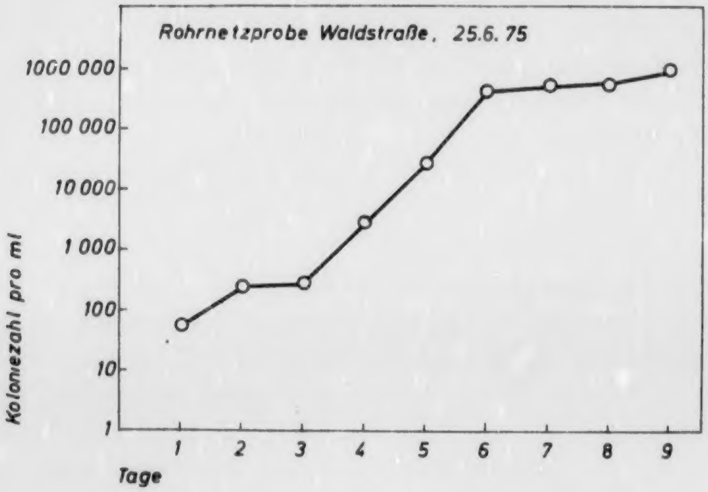


Fig. 1: Germ development in a sample taken from the pipe system

Koloniezahl: bacterical counts per cm^3

Rohrnetzprobe: sample of "Waldstraße", June 25, 1975

Tage: days

form and other chlorinated hydrocarbons (Rook 1974). Although an actual danger to man is not yet proved, this fact is an important additional motive for lowering the content of humic acids in drinking waters.

Experimental results

The experiments at the plant of Fuhrberg may be explained with an example, shown in fig. 2. They were carried out on an experimental filter filled with Lewatit MP 500 A.

Fig. 2

Immediately after regeneration of the resin, about 58 % of the organic carbon (67 % of the permanganate consumption) are removed from the water. With increasing throughput, i.e. with increasing load of the resin, the removal of organic carbon decreases to about 40 % after a throughput of 5000 bed volumes. That means that 5000 m^3 water can be filtered through one m^3 of exchanger material with an average treatment effect of about 50 %, before the next regeneration becomes necessary. A decrease of the organic carbon from 6 to 3 ppm in the Fuhrberg water results in a load of 15 g of organic carbon per litre of resin.

The run, shown in fig. 2 was carried out with the maximum specific throughput, tested during the series of experiments, of 54 bed volumes per hour. These conditions correspond to a contact time of 1.1 minutes and to a filter velocity of 67.5 meters per hour (related to free cross-section, each. Filter length = 1.25 meters).

The treatment effect does not significantly increase with decreasing filter velocity; thus, the planning of an additional treatment stage can be based on high specific throughputs, which correspond to low investment costs. Anyhow, in practice we can expect two effects which are somehow balancing each other: low water consumption corresponds to a high risk of bacterial growth within the untreated water as well as to a better treatment effect during filtration.

Laboratory tests for evaluating the tendency of a water for bacterial growth are fraught with numerous experimental difficulties. However, according to the tests carried out at the Hanover water works, a significant effect of the MP 500 A treatment on the bacterial growth seems to exist.

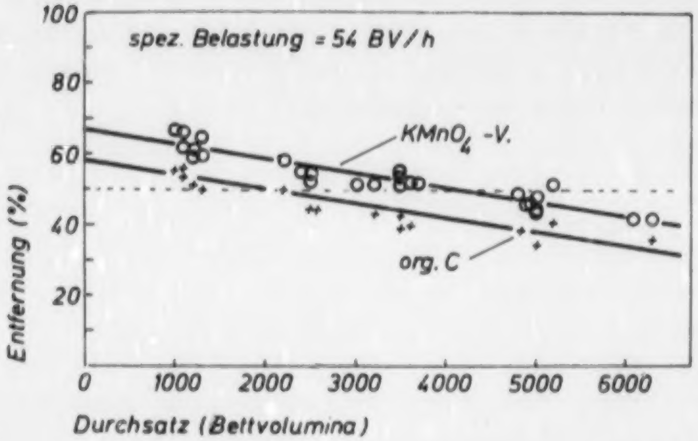


Fig. 2: Percentage removal of organics by MP 500 A filtration as a function of the throughput; data from several regeneration cycles

Entfernung: removal (%)

spez.Belastung: specific throughput = 54 bed vol. per hour

Durchsatz: throughput (bed volumes)
$KMnO_4$-V: $KMnO_4$ consumption

Fig. 3

In fig. 3 the observed number of doublings of the bacterial counts during 24 hours is plotted versus the organic carbon content of the samples. The data are related to the logarithmic growth period of a pure culture of bacteria. The decrease of the tendency of bacterial growth seems to be correlated to the organic carbon concentration of the samples.

Fig. 4

Fig. 4 shows results concerning the problem of chlorine consumption. There is an excellent correlation between chlorine consumption and chemical oxygen demand. This correlation is evident in so far, as both of these phenomena are based on oxidation reactions. In this context it has to be considered, however, that kinetic data (chlorine consumption) are compared with concentrations (chemical oxygen demand). During the experiments the samples contained exceeding free active chlorine. The chlorine consumption during the first hour was not taken into account.

It is obvious that the water from the Fuhrberg plant is an exception compared with the chlorine consumption of the other drinking waters which are distributed by the water works of Hanover. The MP 500 A treatment of the Fuhrberg water has a significant effect which follows the correlation mentioned above.

Despite these positive results the effects of a full-scale plant based on MP 500 A treatment cannot be exactly evaluated with regard to practice. The reason is that under real conditions the transition range between low chlorine concentrations and beginning bacterial growth is of importance. According to experience, this situation is influenced by the condition of the pipe walls to such an extent that its simulation within the laboratory is quite impossible. These questions as well as the optimum disinfection of the optimum disinfection of the water have to be studied in the full-scale range. In addition, we have to expect that also the corrosive properties of the water are changed by MP 500 A treatment, because organic acids are retarding the calcium carbonate precipitation (Rudek 1975). This problem has to be studied intensely, too.

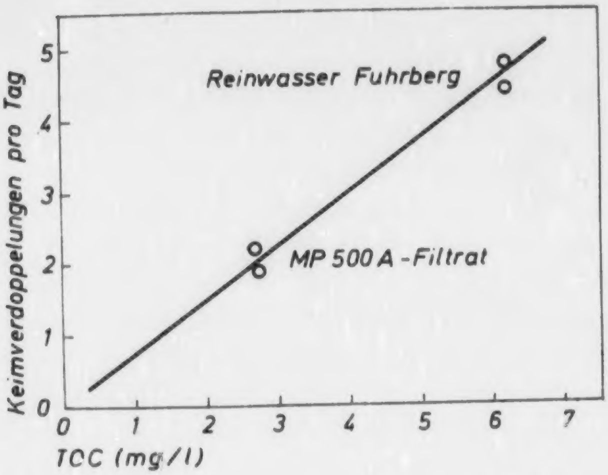


Fig. 3: Effect of MP 500 A - treatment on the rate of germ development during the log. growth period

Keimverdoppelungen: doublings per day

Reinwasser Fuhrberg: drinking water Fuhrberg

MP 500 A-Filtrat: MP 500 A filtrate Fuhrberg

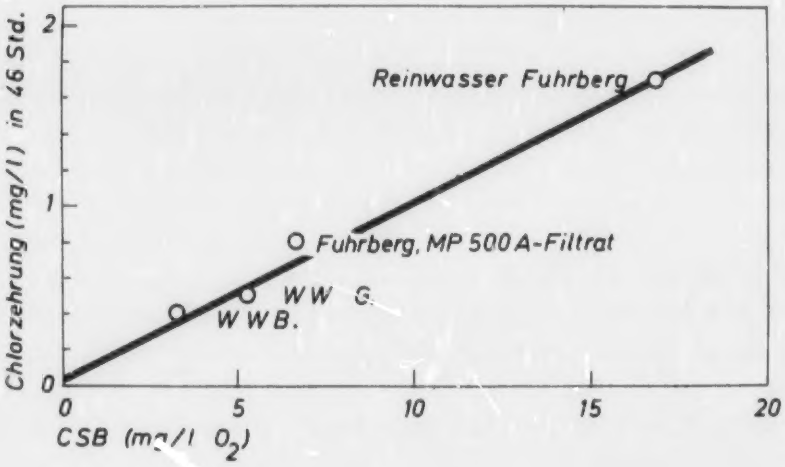


Fig. 4: Consumption of free chlorine as a function of chemical oxygen demand

Chlorzehrung: chlorine consumption (ppm) during 46 hours

Reinwasser Fuhrberg: drinking water Fuhrberg

Fuhrberg MP 500 A-Filtrat: MP 500 A filtrate Fuhrberg

WW G.: plant at Grasdorf

WW B.: plant at Berkhof

CSB (mg/l O_2): COD (ppm O_2)

Regeneration

The regeneration of the exhausted macroporous resin is carried out with a solution containing 100 grams per liter sodium chloride and 20 grams per liter sodium hydroxide. Normally two bed volumes (2 Liters solution per liter of resin) are used. However, according to fig. 5 the regeneration solution can be re-used several times.

Fig. 5

The increase of the organic carbon content of the regeneration solution (in this case up to about 30 grams per liter) does not significantly affect the efficiency of the resin. The ratio between the volumes of treated water and of regeneration waste can be raised under ideal conditions up to 25000 : 1 (tenfold re-use of two bed volumes). In practice, the conditions may be less ideal. It has also be considered that sulphate is enriched in the regeneration solution in a similar way as humic acids. Nevertheless, the volume of regeneration waste is sufficiently small to discuss and study different alternatives for its disposal. The waste needs not necessarily to be discharged into a river. Thermal regeneration and total recycling of the regeneration chemicals were the optimum method with regard to the environment.

Conclusion

The wide-spread opinion "reduced groundwaters" are of minor quality because of their sometimes very high content of iron, manganese, and humic acids, proves to be untrue because, as a rule, they are well-protected genuine groundwaters. When it will be possible to solve the problems of treatment of those waters in a satisfactory and economic way, unused ground-water resources can be opened up which are to some extent already known. In addition, such a treatment technique may get an increasing importance as supplement for already existing techniques to treat surface waters, because a combination of different adsorbents makes excellent treatment effects possible.

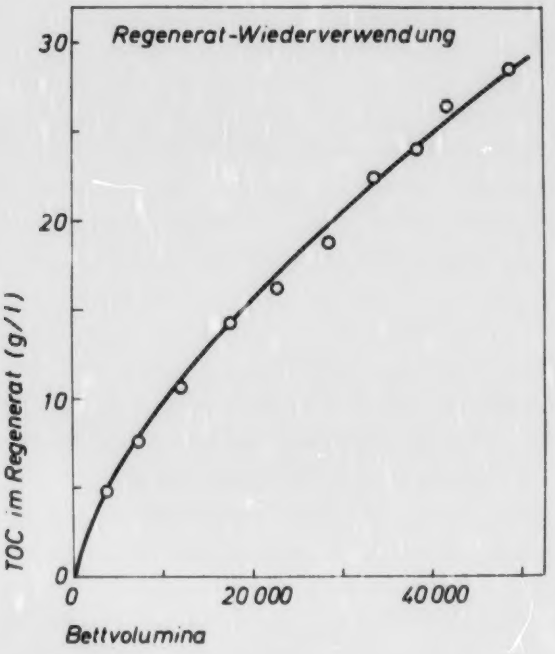


Fig. 5: Increase of organic carbon of the regeneration solution during re-use

TOC im Regenerat: TOC (g/l)

Bettvolumina: bed volumes of the total throughput

Regenerat-Wiederverwendung: Regenerant recycling

THEORY AND PRACTICE IN THE USE OF ADSORPTION PROCESSES

by H. Sontheimer

There are many outstanding experimental studies and theories on the principles of adsorption processes. Despite this fact, an empirical approach is at present preferred in practice, and it is unlikely that this situation will change for some time.

One of the reasons for this discrepancy lies in the fact that all basic work so far has been carried out on simple systems. In practice, rather than a single substance, complex mixtures of dissimilar materials are encountered. At the moment, however, there are still no suitable methods available for their characterization and division into individual groups. This complicates the numerical techniques used in the calculation of adsorption columns.

This is one of the future problems of research work. One possibility for progress lies in the introduction of process-orientated analytical methods, which should be combined in a suitable manner with chemical methods, in particular with group analysis.

During a process-orientated analysis a characterization of the organic substances in the water is carried out, according to the relevant process parameters. The total amount of organics is divided into fractions, for instance depending on the adsorption properties of different adsorbents, or by the kinetics of adsorption on well-characterized adsorbents, or by other appropriate criteria. So far, only suggestions and investigations of suitable analytical methods of this kind have been made. One, for example,is to measure the rate of oxidation under different conditions in order to characterize the organic material in the water (MAIER 1973). The same procedure is more difficult for the adsorption due to the lack of knowledge of the individual processes taking place during adsorption and the frequent occurrence of competitive adsorption. It can be expected, however, that it will be possible in the future to develop suitable methods, the results of which will permit the prediction of the applicability and optimization of the adsorption processes to achieve a satisfactory removal of the substances under investigation.

A further difficulty in the application of adsorption processes lies in the exact definition of the degree of purification desired. Despite the undoubted progress which will be achieved here, it cannot be counted on that one single measuring value will suffice to characterize the process efficiency. Therefore, it will still be necessary in the future to simultaneously control and optimize activated carbon plants with different parameters and methods of investigation.

The criteria which at the moment are especially important for the evaluation of activated carbon filters are set out below:

1) Activated carbon filters should be operated in such a way that the concentration of any organic substance in the effluent water, due to competitive adsorption, must not be greater than in the influent.

2) Activated carbon filters must always have adequate reserve capacities to ensure sufficient effectiveness following a sudden increase in water pollution. It is possible to meet this requirement by measuring the carbon loading at the inlet and outlet of the filter.

3) The concentration of non-polar organo-chloro compounds, if present in the raw water, should be reduced as far as possible, and should not exceed 10 μg/l.

4) The following additional requirements should be met by the filter:

   a) removal of taste and odour
   b) removal of heavy metals
   c) adequate biological performance, if desired
   d) lowering of the total concentration of dissolved organics

The last-mentioned requirement has the advantage that it is easy to control and measure, e.g. by UV extinction. Provided sufficient experience is available, it has the additional advantage that it may be correlated with the other criteria when using the same raw water.

The above specifications clearly illustrate that it is essential to deal more thoroughly with the criteria to be used for evaluating the effectiveness of activated carbon filters. The methods suitable for this purpose, which will not be gone into detail here, should not only be rapid and automatic if possible, they should also be orientated towards the aim of the treatment and supply sufficient process information so that an optimum operation can be guaranteed.

Important for the future is also the optimization of the pre- and posttreatment combined with the adsorption process. Practical experience shows that a considerable improvement in the effectiveness of treatment plants can be achieved when the various treatment processes are coordinated.

Considering the increase in the variety of applications of adsorption processes, the use of activated carbon filters for biological purification is of special importance. The degree of purification achieved with this process technique allows a partial replacement of the commonly used ground- and slow sand filtration. Furthermore, it is important for the future that more specific adsorbents are developed which are able to remove - either on their own or in mixtures with other adsorbents - as much as possible of the particularly undesirable components. Such a development is dependent on a more thorough study of the fundamental processes of adsorption. In particular, more detailed information on the influence of chemical parameters on adsorption, especially during the adsorption of mixtures of substances, is required. In addition, we still lack sufficient knowledge of the accessibility of the different pore systems in an activated carbon filter, for a useful description of the adsorption kinetics.

The specific, or rather the general adsorbent characteristics of activated carbon are of importance also for the most advantageous placement of the adsorption process into the total scheme of water treatment, whereby special attention is paid to an optimum utilization of the specific adsorption characteristics.

The mention of some research work which is of particular importance in the near future is meant to show that the development in this sector of adsorption has by no means been concluded yet.

It was the aim of this course of lectures to summarize the information and practical experience available so far in the field of adsorption during drinking water treatment, paying special attention to practical aspects. By this it was hoped to pass on to others useful knowledge when applying this method of treatment. When practical experience is combined with a thorough knowledge of the basic process data, it will be possible to achieve still better results in drinking water treatment. It will then be possible to guarantee the supply of drinking water of excellent quality at any time, even under difficult conditions.

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